

# KINGZETT'S CHEMICAL ENCYCLOPÆDIA

A DIGEST OF CHEMISTRY AND ITS INDUSTRIAL APPLICATIONS

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## FOREWORD

CHEMISTRY, Pure and Applied, covers a vast territory of knowledge, and no man can have a specialized knowledge of more than one corner of it. Very few men have, in fact, more than a smattering of knowledge of any considerable part of the subject. But at times we all need to travel beyond our narrow strip and in the great majority of such excursions we only want to pay a casual call.

The extent of the information we may reasonably expect from an encyclopædia clearly depends on the scope of that work. It may well be thought, the larger the better, and yet there is a certain danger inherent in the more ambitious productions; and I am able to give an example of this, for these words would not have been written if their author had never been encouraged to pursue the study of chemistry, a matter which was closely connected with the use of an encyclopædia,

My father was a pioneer manufacturer, the first to make lint and bandage by machinery; and he was fond of doing everything for himself. In due course he attacked the problem of bleaching, and found the subject treated at length in a popular and greatly respected cyclopædia of considerable dimensions. The result was that he determined that one of his sons should study chemistry.

It is probable that the more useful encyclopædia are those of the one-volume type of convenient size. One such, produced under the auspices of a large chemical industry, is very frequently consulted in our household, and not exclusively for the solution of crossword puzzles.

Kingzett is essential to a chemist engaged in any administrative capacity whose interest and contacts are over an extensive range of subjects. It is a handy book of reference for executives in the chemical industry whether in sales, production, or research, and it is equally necessary to the Professor and the government official. The place for it is not on the shelves but on the working desk.

Kingzett makes no pretences of being a substitute for a library, but it does at least put one quickly on the track of deeper reading, and in a very large number of cases it supplies all the information that is needed. For example, a very useful feature is the explanation of trivial names. No amount of scientific knowledge will help you if you are told to use Abrac (p. 1) and you are unaware that this is a glycerine resin ester (see Gums and Resins). Applying tests for completeness in this respect, I found that Kingzett scored high, though naturally not full marks.

Turning over the pages some really excellent summaries of topical interest are encountered. Such are the articles on penicillin and on streptomycin treated from several angles ; there are others on sugar, and on rubber, natural and synthetic. These admirable brevities are not all concerned with substances or materials ; they deal also with topics such as infra-red spectroscopy, chromatography, and even chemical engineering and economic aspects, to mention a few at random. All such reviews—and there are many of them—are well documented. The further reading recommended is the best so far as my knowledge of the matter goes.

Browsing in a dictionary is a fascinating occupation whether it be to trace the incredible relationships of classical mythology, or to discover strange archaisms and gaps in one's knowledge of the language, or even as a chemist to skim through the pages of Kingzett and glance over the wall at our neighbour's garden. The act will doubtless promote a proper feeling of humility and a determination to do better in our own cultivation. But it will also convince us of the value of wider knowledge.

In my opinion this new edition more than maintains the fine traditions handed on by its predecessors and is clearly the result of the collaboration of experts in many departments of the subject. Every effort seems to have been made to bring it right up to date. The Editor and contributors may be sincerely congratulated on a near approach to the accomplishment of an almost impossible task.

We now have a good nucleus which can be later improved by deletions and additions. May I conclude with an expression of the hope that the latter will never reach such proportions as to alter the character of this epitome of chemical science and technology ?

ROBERT ROBINSON



EXTRACT FROM  
PREFACE TO THE THIRD EDITION  
INCLUDED FOR ITS HISTORICAL INTEREST

WHEN the Great War came in 1914, and the Government looked to our chemists to make good its neglect of many years, in order to overtake the tremendous advancements made and utilized by the aggressor nation, Germany, I set myself two tasks, which, being performed, might help to popularize the study of chemistry and advance its applications to industry within the Empire. One of these tasks was the production of my little work entitled *Chemistry for Beginners and School Use* (Baillière, Tindall and Cox). The other task was a more ambitious one, and, while it has been a labour of love, it has proved a somewhat exhaustive one—viz., the production of this Encyclopædia, which is unique in character and now makes its appearance in the third edition under a new title. *My aim has been to prepare an epitomized digest of chemistry and its industrial applications, in a form which should be useful as a work of reference by all classes of the community.*

C. T. KINGZETT





# ALPHABETICAL LIST OF CHEMICAL SYMBOLS WITH NAME AND ATOMIC NUMBER OF CORRESPONDING CHEMICAL ELEMENTS

Chemical Symbol	Chemical Element	Atomic Number	Chemical Symbol	Chemical Element	Atomic Number
A	Argon	18	Mg	Magnesium	12
Ac	Actinium	89	Mn	Manganese	25
Ag	Silver (Argentum)	47	Mo	Molybdenum	42
Al	Aluminium	13	N	Nitrogen	7
Am	Americium	95	Na	Sodium (Natrium)	11
As	Arsenic	33	Nb	Niobium (Columbium)	41
At	Astatine	85	Nd	Neodymium	60
Au	Gold (Aurum)	79	Ne	Neon	10
B	Boron	5	Ni	Nickel	28
Ba	Barium	56	Np	Neptunium	93
Be	Beryllium (Glucinum)	4	O	Oxygen	8
Bi	Bismuth	83	Os	Osmium	76
Br	Bromine	35	P	Phosphorus	15
C	Carbon	6	Pa	Protactinium	91
Ca	Calcium	20	Pb	Lead (Plumbum)	82
Cb	Columbium See Niobium		Pd	Palladium	46
Cd	Cadmium	48	Pm	Promethium	61
Ce	Cerium	58	Po	Polonium	84
Cl	Chlorine	17	Pr	Praseodymium	59
Cm	Curium	96	Pt	Platinum	78
Co	Cobalt	27	Pu	Plutonium	94
Cr	Chromium	24	Ra	Radium	88
Cs	Cesium	55	Rb	Rubidium	37
Ct	Celtium. See Hafnium.		Re	Rhenium	75
Cu	Copper (Cuprum)	29	Rh	Rhodium	45
D	Deuterium (Hydrogen of mass 2)	1	Rn	Radon	86
Dy	Dysprosium	66	Ru	Ruthenium	44
Er	Erbium	68	S	Sulphur	16
Eu	Europium	63	Sb	Antimony (Stibium)	51
F	Fluorine	9	Sc	Scandium	21
Fe	Iron (Ferrum)	26	Se	Selenium	34
Fr	Francium	87	Si	Silicon	14
Ga	Gallium	31	Sm	Samarium	62
Gd	Gadolinium	64	Su	Tin (Stannum)	50
Ge	Germanium	32	Sr	Strontium	38
Gl	Glucinum. See Beryllium.		Ta	Tantalum	73
H	Hydrogen	1	Tb	Terbium	65
He	Helium	2	Tc	Technetium	43
Hf	Hafnium (Celtium)	72	Te	Tellurium	52
Hg	Mercury (Hydrargyrum)	80	Th	Thorium	90
Ho	Holmium	67	Ti	Titanium	22
I	Iodine	53	Tl	Thallium	81
In	Indium	49	Tm	Thulium	69
Ir	Iridium	77	U	Uranium	92
K	Potassium (Kalium)	19	V	Vanadium	23
Kr	Krypton	36	W	Wolfram (Tungsten)	74
La	Lanthanum	57	Xe	Xenon	54
Li	Lithium	3	Y	Yttrium	39
Lu	Lutetium	71	Yb	Ytterbium	70
			Zn	Zinc	30
			Zr	Zirconium	40

For other data see chart opposite; Elements; and the individual elements.

## EXPLANATORY NOTES

### ABBREVIATIONS.—

Acet. v.	means acetyl value.
acid v.	„ acid value.
atm.	„ atmospheres (pressure units).
A.U.	„ Angström Unit.
Bé.	„ Baumé.
b.p.	„ boiling point.
B.Th.U.	„ British Thermal Units.
cal.	„ calories.
d.	„ density.
d.	„ dextro-rotatory.
f.p. or fr. p.	„ freezing point.
g., gm.	„ gram.
i.v.	„ iodine value.
l.	„ levo-rotatory.
m.p.	„ melting point.
N.O.	„ Natural Order.
opt. rot.	„ optical rotation.
ref. ind.	„ refractive index.
r.p.	„ rotatory power.
sap. v.	„ saponification value.
sp. gr.	„ specific gravity.
Tw.	„ Twaddell.

NOTE.—For other abbreviations see Frontispiece; and Weights and Measures.

*B.C.A.* : *British Chemical Abstracts* :  
A, Pure Chemistry; B, Applied  
Chemistry.  
*Biochem. J.* : *Biochemical Journal* (Cam-  
bridge University Press).  
*Brit. Med. J.* : *British Medical Journal*.  
*Brit. Pharm.* } *British Pharmacopœia*.  
B.P.  
*C. and D.* : *Chemist and Druggist*.  
*Chem. Age* : *Chemical Age*.  
*Chem. Eng.* : *Chemical Engineering*  
(New York).  
*Chem. Eng. News* : *Chemical and En-  
gineering News* (American Chemical  
Society).  
*Chem. and Ind.* : *Chemistry and Indus-  
try* (Society of Chemical Industry).  
*Chem. and Met. Eng.* : *Chemical and  
Metallurgical Engineering*.  
*Chem. News* : *Chemical News*.  
*Chem. Rev.* : *Chemical Reviews* (American  
Chemical Society).  
*C.T.J.* : *Chemical Trade Journal*.  
*Ind. Chem.* : *The Industrial Chemist*.  
*Ind. Eng. Chem.* : *Industrial and En-  
gineering Chemistry*.  
*J. Amer. C. S.* : *Journal of the American  
Chemical Society*.  
*J. Biol. Chem.* : *Journal of Biological  
Chemistry*.  
*J.C.S.* : *Journal of Chemical Society*.  
*J.C.S. Abs.* : *Journal of Chemical Society  
Abstracts*.  
*J. Chem. Educ.* : *Journal of Chemical  
Education* (American Chemical  
Society).  
*J. Inst. Chem.* : *Royal Institute of  
Chemistry Journal*.  
*J. Phys. Chem.* : *Journal of Physical  
Chemistry*.  
*J.S.C.I.* : *Journal of the Society of  
Chemical Industry*.  
*Pharm. Journ.* } *Pharmaceutical Journal*.  
*Pharm. J.*  
*Trans. Inst. Chem. Engrs.* : *Transactions  
of the Institution of Chemical Engineers*.  
(London).

CRYSTAL SYSTEMS.—References to crystal systems are to be inter-  
preted by the classification given in the article on "Crystals and  
Crystallization."

PROPRIETARY ITEMS.—These names are expressed in inverted commas.

# KINGZETT'S

## CHEMICAL ENCYCLOPÆDIA

**A-BOMB** — See Nuclear Chemistry.

**ABIETIC ACID** ( $C_{20}H_{30}O_2$ ) — A diterpene carboxylic acid and a constituent of common rosin (colophony) which crystallizes in small plates, of acid v. 183·7, soluble in hot alcohol, ether, strong acetic acid, and chloroform; and m.p. 182° C. It can be obtained in a 50 per cent. yield by distillation of rosin at 200° to 210° C. 1 mm. (bath 255° C.), followed by crystallization from methyl alcohol or acetone. According to Dupont and Desalbres, well-defined abietates of various metals have been obtained in alcoholic solutions, alkali metals giving crystalline salts corresponding to a formula of  $3C_{20}H_{30}O_2 \cdot C_{20}H_{20}O_2 \cdot M$ . Potassium abietate is a reddish-brown viscous paste soluble in cold water for use in place of rosin-soaps. Abietic acid is converted by oxidation with selenium oxide and subsequent dehydration into dehydroabietic acid. Alpha-pyroabietic acid is a mixture of de-, di-, and tetra-hydroabietic acids. Dihydroabietic acid is obtained by hydrogenation of abietic acid with a platinum catalyst (Lombard, 1939), and tetrahydroabietic acid similarly with a Raney nickel catalyst. (See *Natural Products Related to Phenanthrene*, by Fieser and Fieser (Reinhold Publishing Corp., New York); also Gums and Resins.)

“**ABRAC**” — A glycerine resin ester, of m.p. about 100° C., and not exceeding acid value 5. It is pale in colour, and has an ash content less than 0·1 per cent. (See Gums and Resins.)

**ABRASIVES** — Preparations such as “Aloxite,” “Alundum” (crystallized aluminium oxide), “Carborundum” (silicon carbide), “Cryston” (silicon carbide), “Corubin,” corundum, “Diamantine” (aluminum oxide), emery, garnet, “Glassite” (black oxide of iron), lime, rouge, kieselguhr, pumice powder, sand, sandstone, “Sira,” tripoli, oilstone, and whetstone, used for cleaning or abrading by rubbing.

Hydrated magnesium silicates of the serpentine type, containing 3·5 per cent. iron, when calcined at a red heat and subsequently ground, are stated to produce useful abrasives.

Diamond-crushed steel, prepared from white-hot crucible steel and crushed cast iron by quenching, is used as an abrasive for cutting granite, marble, and glass.

Emery, a native hard form of alumina coloured with oxides of iron and manganese, in the raw state comes from the Island of Naxos, in the Greek Archipelago (see Corundum); silicon carbide, corundum,

and corundite are found in South Africa ; and an aluminous abrasive is found in the south of France and the Pyrenees. All are used in making grinding-wheels, polishing, etc.

"Carborundum" and "Alundum" (electric furnace products) are important industrially-prepared abrasives. "Alundum" is a form of aluminium oxide ( $Al_2O_3$ ) made by fusing bauxite in the electric furnace ; m.p. approximately  $1,750^\circ$  to  $2,100^\circ C.$ , and sp. gr. about 4.0. "Aloxite" is another form of the same substance prepared by fusion of bauxite. "Carborundum" (SiC) is a greenish blue-black crystalline silicon carbide of sp. gr. 3.12-3.20 largely used by reason of its great hardness (ranking in this character next to the diamond) for grinding and cutting metals in engineering shops. It is made, of various degrees of purity up to 99.5 per cent. and graded between 20 and 100 mesh screens, by heating a mixture of silica, fine sand, and finely ground petroleum coke with a little salt and sawdust in an electric furnace, using a current of 10,000 amperes. In this way a ring of crystals is built up surrounding the core. "Cryston" is another product of the same composition.

N.B. — The name "Carborundum" is the registered trade mark of the make of silicon carbide of the Carborundum Company of Niagara Falls, in Canada, Australia, New Zealand, and the U.S.A., but the name is not registered in Great Britain.

In the electroplating industry, rottenstone, tripoli, pumice, and emery are the more important abrasives employed.

Borides, carbides and nitrides of some of the heavier elements offer prospect of specialized applications. The accompanying table presents some of the data on hardness and melting points of these abrasives.

#### ABRASIVES—THE BORIDES, CARBIDES AND NITRIDES FROM TITANIUM TO TUNGSTEN

*Table showing Hardness and Melting Points*

Hardness, Mohs' Scale : Diamond, 10 ; Corundum, 9 ; Topaz, 8 ; Quartz, 7 ; Melting Point (M.P.) in  $^\circ C.$ , approximate

	Boride		Carbide		Nitride	
	Hardness	M.P.	Hardness	M.P.	Hardness	M.P.
Titanium .. ..	>9		>8	3150	>8	2950
Vanadium .. ..	>9		>9	2830		2050
Chromium .. ..	8		>7	1890		
Zirconium .. ..	>9	3000	>8	3530	>8	2980
Columbium .. ..	>9			3500	>8	
Molybdenum .. ..	>9		7-9	2700		
Hafnium .. ..		3060		3900		
Tantalum .. ..	>9		>9	3875	>8	3100
Tungsten .. ..	>9		>9	2850		

For most grinding purposes the graded grains of abrasive are bonded together with a vitrified binder to form grinding wheels. For hand use the grains are affixed to paper or cloth by means of a binder, such as

Cerium oxide is a preferred abrasive in the optical glass industry, where ferric oxide also has long been used.

**ABSORPTION** — The physical soaking up of one substance into another ; distinct from adsorption. (See “ Absorption of Gases in Spray Towers,” by A. W. Hixson and C. E. Scott (*Ind. Eng. Chem.*, **27**, 311 (1935)) ; Absorption and Extraction Symposium, *Ind. Eng. Chem.*, **29**, 270 *et seq.* ; 514 *et seq.* (1937) ; *Absorption and Extraction*, by T. K. Sherwood (McGraw-Hill Book Co., New York) ; and Gas Absorption).


**Ac** — A symbol used for acetyl ( $\text{CH}_3\cdot\text{CO}-$ ) radical.

**ACANTHITE** — Natural silver sulphide ( $\text{Ag}_2\text{S}$ ), of sp. gr. 7.25 and crystal system No. 1, containing 87 per cent. silver, found in Colorado.

In nuclear chemistry, accelerators are instruments such as cyclotrons or betatrons used to accelerate particles to high velocity. (See Nuclear Chemistry.)

**ACCUMULATORS (Storage Batteries)** — See Electricity.

**ACENAPHTHENE**  $\left( \text{C}_{10}\text{H}_6(\text{CH}_2)_2, \begin{array}{c} \text{H}_2\text{C} - \text{CH}_3 \\ | \quad | \\ \text{---} \text{---} \end{array} \right) - \text{An}$  intermediate dye-

and at red heat loses hydrogen to form acenaphthylene, 

a yellow solid of m.p. 93° C. Some of its derivatives are suitable for the production of intermediates utilizable in making dyes and therapeutic compounds. The nitration, sulphonation, and halogenation of this body take place most readily in the *para* positions with respect to the two methylene groups. (See Fieser and Kilmer, *J. Am. Chem. Soc.*, **62**, 1354 (1940).)

**ACETAL** ( $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)_2$ ) — A colourless, volatile solvent liquid of sp. gr. 0.831, b.p.  $104^\circ\text{C}$ .; made by partial oxidation of ethyl alcohol; soluble in water, alcohol, and ether.

**ACETALDEHYDE** ( $\text{CH}_3\text{CHO}$ ) — Acetaldehyde is commonly known as "aldehyde" and otherwise as "ethanal," and is ordinarily prepared by the oxidation of ethyl alcohol by means of potassium dichromate or manganese dioxide and sulphuric acid. By the commercial process it is made by passing acetylene into dilute sulphuric acid containing a small proportion of mercury sulphate. It is a colourless, mobile, inflammable, volatile fluid of a peculiar pungent odour, of b.p.  $20^\circ\text{C}$ . and sp. gr. 0.783; miscible with water, alcohol, and ether, and possesses strong reducing properties. (See Reducing Agents.) Apart from its chemical applications, it finds use as a solvent; as an antiseptic inhalant in cases of nasal catarrh and ozæna. It has been shown by the Food Investigation Board that healthy fruit can be treated with concentrations of it strong enough to destroy fungal spores and fungal mycelium, without ill-effects on the fruit. (See Report for 1929; Acetylene Industries, Chart I; H. D. Foster and D. B. Keyes on "Catalysts for the Vapour Phase Oxidation of Acetaldehyde" (*Ind. Eng. Chem.*, **29**, 1254 (1937)).)

**ACETALS** — Compounds resulting from the combination of two alcohol molecules with one of an aldehyde or ketone through the loss of one molecule of water—the dialkyl ethers of hypothetical 1, 1-dihydroxy compounds. The process of formation is known as *acetalization*. These compounds are important in synthetic work as they are usually more stable to oxidation than the parent aldehyde or ketone.

**ACETAMIDE** — See Amides.

**ACETANILIDE (Phenylacetamide)** ( $\text{C}_6\text{H}_5\text{NH.CO.CH}_3$ ) — A white crystalline intermediate of m.p.  $114^\circ$  to  $116^\circ\text{C}$ . known under the pharmaceutical name of "Antifebrine," and used in medicine as an antipyretic. It is readily soluble in hot water, alcohol, ether, and chloroform, and is made by boiling aniline with glacial acetic acid.

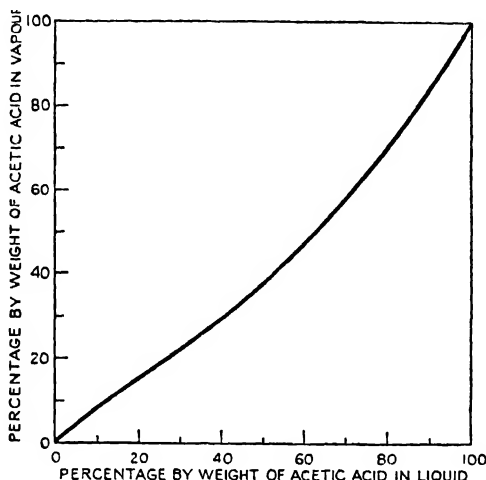
**ACETARSOL ("Devegan," "Orarsan," "Stovarsol")** ( $\text{C}_8\text{H}_{10}\text{O}_6\text{Na}$ s) — A white, crystalline compound, namely, 3-acetylamino-4-hydroxyphenylarsonic acid; almost insoluble in water and alcohol; m.p.  $245^\circ\text{C}$ . Used in medicine for the treatment of syphilis, amœbic dysentery, and trichomonal infections.

**ACETATES** — See Acetic Acid.

**ACETIC ACID** ( $\text{CH}_3\text{COOH}$ ) — The active principle of vinegar, which contains from 3 to 5 per cent. It is readily prepared by the oxidation of ordinary alcohol and the fermentation of alcoholic liquids by the organism *Mycoderma aceti*. It is also extracted from the products of the dry distillation of wood. The acid is converted into calcium acetate by treatment with lime, and the resulting calcium acetate subsequently treated with hydrochloric or sulphuric acid, the free acetic acid being finally obtained by distillation or it is extracted direct from the crude pyroligneous liquor by means of ether; in another, ethyl acetate is used, while the "Suida" process employs a high boiling wood oil, the acetic acid being recovered from the oil by

vacuum distillation. See D. F. Othmer on "Separation of Water from Acetic Acid by Azeotropic Distillation" (*Ind. Eng. Chem.*, **27**, 250 (1935)). The principal patents in this field are Oxley and Fallows (to Celanese Corp. of America) U.S. Patent, 1,936,172 (Nov. 12, 1933), Lunt (to E. B. Badger and Sons Co.), U.S. Patent 1,958,898 (May 15, 1934), and Ricard and Guinot (to *Soc. Anon. Usines de Melle*), U.S. Patent, 1,959,547 (May 22, 1934).

ACETIC ACID ( $\text{CH}_3\text{COOH}$ )—WATER ( $\text{H}_2\text{O}$ ) MIXTURES  
VAPOUR-LIQUID RELATIONSHIP AT BOILING-POINT  
(PRESSURE : 760 MM. HG)



What is known as the "quick process" of producing ordinary acetic acid consists in trickling dilute alcoholic liquors over shavings of beechwood previously coated with "mother of vinegar"—that is, a cultivation of the *Mycoderma aceti*—at a temperature of 35° C. The souring of thin wines is due to the production of acetic acid by the same micro-organisms, which are always present in the air. (See Vinegar.)

The process for the production of acetic acid from acetylene is as follows: calcium carbide is prepared by heating lime with coke in an electric furnace, and the acetylene produced from this product is then combined with water, through the agency of sulphuric acid acting in conjunction with mercuric and ferric sulphates, whilst the resulting acetaldehyde is oxidized by oxygen distilled from liquefied air.

Pure acetic acid (glacial acetic acid) is a corrosive crystalline body of sp. gr. 1.055 at 15° C., m.p. 16.7° C., b.p. 118° C., miscible with water and with alcohol.

Acetic acid in its various forms finds large application as a food preservative and flavouring material, also in many industrial processes,

including the manufacture of cellulose acetate, white-lead, and the treatment of rubber latex. For technical purposes it is marketed as a water solution containing respectively 40, 60, and 80 per cent. of acetic acid.

By combination with bases, acetic acid forms the salts known as acetates, most of which, including all the normal ones, are soluble in water. (See "The Acetates in Industry," by C. H. Butcher (*C.T.J.*, **89**, 151, 179 (1931)); Pyroligneous Acid; Vinegar, and various Metals and Organic Radicals for acetates.)

**ACETIC ANHYDRIDE** ( $(\text{CH}_3\text{CO})_2\text{O}$ )—A colourless mobile liquid of sp. gr. 1.082 at 20° C. and suffocating odour, which boils at 139.6° C. It can be obtained by distilling acetyl chloride with an alkali acetate, but is mainly made by the action of sulphur chloride on anhydrous sodium acetate, and may be chemically regarded as derived from acetic acid by the abstraction of a molecule of water from two molecules of the acid— $2\text{CH}_3\text{COOH} - \text{H}_2\text{O} = (\text{CH}_3\text{CO})_2\text{O}$ . It is used for acetylation of amines and phenols, in making aeroplane dope and cellulose acetate plastic, is soluble in alcohol and ether, and resolved by water into acetic acid.

**ACETIC ETHER** — See Ethyl Acetate under Esters.

**ACETIN (Monoacetin)** ( $\text{C}_3\text{H}_5(\text{OH})_2\text{OCOCH}_3$ )—A colourless, thick liquid of sp. gr. 1.221, prepared by heating glycerol and glacial acetic acid; soluble in water, alcohol, and ether; used for gelatinizing smokeless gunpowder and dynamite, and as a solvent for slightly soluble dye-stuffs, particularly induline base. (See Glycerol, and Triacetin.)

**ACETOMENAPHTHONE** ( $\text{C}_{15}\text{H}_{14}\text{O}_4$ )—A white, crystalline, synthetic orally active homologue of vitamin K, namely, 1,4-diacetoxy-2-methylnaphthalene; almost insoluble in water; slightly soluble in alcohol; m.p. 112° to 114° C (See Vitamins (Vitamin K).)

**ACETONE (Dimethyl Ketone)** ( $\text{CH}_3\text{COCH}_3$ )—A mobile, inflammable, colourless liquid of agreeable characteristic odour, obtained, amongst other methods, by the dry distillation of calcium acetate in a stream of inert gas (nitrogen or carbon dioxide) at 450° to 490° C. It is made in the U.S.A. from isopropyl alcohol derived from propylene from natural or cracked petroleum gas.

To produce acetone from glacial acetic acid, the latter is vaporized and passed through a heated vessel or steel tubes containing a catalyst which effects its decomposition, as expressed by  $2\text{CH}_3\text{COOH} = (\text{CH}_3)_2\text{CO} + \text{CO}_2 + \text{H}_2\text{O}$ . A yield of up to 95 per cent. is obtained by passing the preheated vapour over granulated calcium oxide mixed with a small amount of magnesia at 483° C. The resultant vapours from the tubes are scrubbed in a soda-tower to remove any unchanged acetic acid and the acetone is subsequently rectified by distillation. For recovering acetone vapour from the air by scrubbing operations, strong sulphuric and phosphoric acids are stated to effect almost perfect absorption. (See W. R. Ormandy, *B.C.A.*, B, 1930, 49.)

There are also biochemical (bacterial) processes for the production

## ACETONE — ACETYLENE

of acetone in association with butyl and ethyl alcohols (in the proportions of 3 to 6 to 1 respectively, attended by evolution of carbon dioxide and hydrogen) from cooked corn starch under aseptic conditions. In Weizmann's process the particular species of bacillus employed is known as "BY" or *clostridium acetobutylicum*. (See Lecture by J. V. Eyre (*Inst. Chem.*, November, 1931) on Fermentation Industries, p. 19; and Fermentations.)

It is miscible with many other commercial solvents, and is largely used in the manufacture of explosives, and chloroform, also as a solvent of guncotton, celluloid, and wood-tar bodies; it boils at 56.5° C., and has a sp. gr. of 0.792 at 20° C. Chemically, it belongs to a series of "ketones," and it is said to be present in urine in small quantity. (For other details of its properties, see *J. Amer. Chem. Soc.*, November, 1926; see also "Acetone," by L. C. Cooley (*Ind. Eng. Chem.*, **29**, 1399 (1937)); Acetic Acid, and Ketones.)

**ACETOPHENETIDIN** — See Phenacetin.

**ACETOPHENONE** ( $C_6H_5.CO.CH_3$ ) — A white, crystalline body, m.p. 20.5° C., b.p. 202° C., made from benzene by treatment with acetyl chloride in presence of anhydrous aluminium chloride; soluble in alcohol and ether, and used in perfumery.

"**ACETOSAL**" — See Acetylsalicylic acid.

**ACETYL** ( $CH_3CO-$ ) — An organic radical derived from acetic acid.

**ACETYLARSAN** — An organic compound of pentavalent arsenic, namely, diethylamine-3-acetyl-amino-4-hydroxyphenylarsonate, soluble in water. Used for the treatment of syphilis, particularly for children.

**ACETYL CHLORIDE** ( $CH_3.COCl$ ) — A colourless mobile liquid which boils at 55° C., and has a suffocating odour. It is used in the acetylation of alcohols, phenols, and amines.

**ACETYLCHOLINE** ( $((CH_3)_3N(OH)CH_2.CH_2.O.CO.CH_3)$ ) — A white, hygroscopic, crystalline compound possessing a bitter, saline taste; formed locally in the tissues from choline in response to stimulation of the parasympathetic nerve endings and said to possess a physiological activity about 100,000 times greater than that of choline. (See A. J. Clarke, *Chem. and Ind.*, **49**, 533 (1930); *The Pharmacological Basis of Therapeutics*, by L. Goodman and A. Gilman (Macmillan, New York).)

**ACETYL VALUES** — See Fats.

**ACETYLATION (Acetylation)** — The introduction of the acetyl radical ( $CH_3CO-$ ) into compounds, such as alcohols, phenols and amines, by the action of acetic anhydride, acetyl chloride, or glacial acetic acid.

**ACETYLENE BLACK** — Made by burning acetylene against a cooled metal surface, as also by several chemical processes. (See Carbon Black.)

**ACETYLENE (Ethyne)** ( $CH:CH$ ) — A colourless, odorous, and poisonous hydrocarbon gas of sp. gr. 0.91 (Air=1.00) produced from calcium

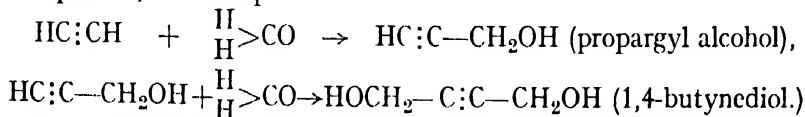
carbide by action of water:  $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{Ca(OH)}_2 + \text{C}_2\text{H}_2$ . It is soluble in water, alcohol, and acetone, and is of heating value 1455 B.Th.U. per cu. ft. By burning it in conjunction with oxygen in blow-pipe form, a very high temperature is attained—higher, indeed, than that of the oxyhydrogen flame—and used as a means for cutting through armour-plates up to 6 inches in thickness even when under water. Just above the top of the luminous cone the temperature has been determined as about  $3,100^\circ\text{C}$ . So-called “dissolved acetylene” is acetylene compressed in a cylinder containing a suitable porous material soaked in acetone, a solvent which absorbs a large quantity of acetylene under pressure (300 volumes of acetylene in 1 volume of acetone at 12 atmospheres’ pressure) and gives off the gas freely when the pressure is released, thus qualifying it to be safely transported and used. Acetylene in contact with copper forms copper acetylide, a compound which readily detonates upon friction. Silver acetylide and sodium acetylide are also known. Acetylene is used also as an illuminant in a burner specially designed to incorporate a large proportion of air.

The reactivity of acetylene renders it very useful in many chemical syntheses (see accompanying charts) based on its initial transformation into acetaldehyde or into chloro-derivatives. Nieuwland used the catalyst  $\text{Cu}_2\text{Cl}_2, \text{NH}_4\text{Cl}, \text{HCl}$  to carry out the transformations shown in Part II of the chart. During World War II, Reppe and associates, in Germany, extended the safe applications of acetylene in chemistry, in large part (1) by using special catalysts; (2) by working under pressures up to 15 atmospheres; (3) by having nitrogen gas present as a diluent; and (4) by stuffing all large pipes with bundles of tubes whose diameters are one-half inch or less. The variations that were examined resulted in three major types of reaction, namely,

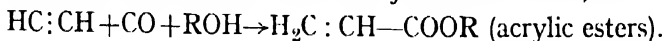
(1) **Vinylation**, where the special catalyst is a potassium salt, whereby alcohols, acids, phenols, glycols, sugars, amines, and mercaptans are converted into vinyl derivatives at  $160^\circ$  to  $185^\circ\text{C}$ ., for example:



(2) **Ethynylation**, where the special catalyst is usually copper acetylide, whereby carbonyl compounds are converted into triple-bond addition compounds, for example:



(3) **Carboxylation**, where the special catalyst is nickel carbonyl, whereby acid derivatives are obtained by addition of CO, for example:

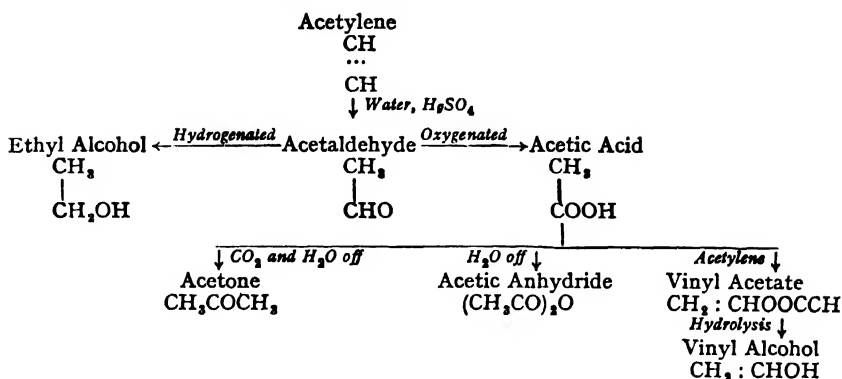


## ACETYLENE INDUSTRIES

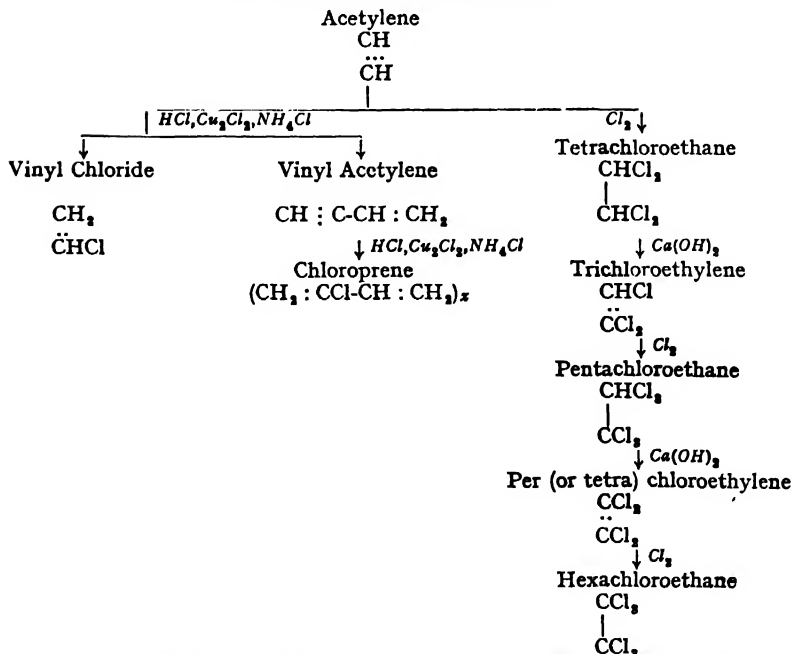
## CHARTS SHOWING PRINCIPAL RELATIONSHIPS

Arranged by the Editor.

## I. Oxygen-Function Derivatives



## II. Chlorine-Function Derivatives



See Solvents for further information concerning some of these substances.

Vogt (Reinhold Publishing Corp., New York); *The Chemistry of Acetylene and Related Compounds*, by E. D. Bergmann (Interscience Publishers, New York); *Acetylene and Carbon Monoxide Chemistry*, by John W. Copenhaver and M. H. Bigelow (Reinhold Publishing Corp., New York); *Acetylene Homologues and Derivatives*, by Pierre Pagaiol (Mapleton House, Brooklyn); Oxy-acetylene Flame, Rubber (Substitutes), Solvents, and Welding.

**ACETYLENE TETRACHLORIDE** ( $\text{CHCl}_2\cdot\text{CHCl}_2$ ) — See Tetrachloroethane.

**ACETYSALICYLIC ACID** ("Acetosal", "Aspirin") ( $\text{C}_6\text{H}_4(\text{O}\cdot\text{CO}\cdot\text{CH}_3)\text{COOH}$ )—A white crystalline powder of m.p.  $135^\circ$  to  $138^\circ$  C, prepared by the action of acetic anhydride or acetyl chloride on salicylic acid. Used in medicine as an analgesic and antipyretic. Soluble in alcohol and ether but only slightly soluble in water.

**ACICULAR (Crystals)** — Needle-shaped.

**ACID, ANDRESEN'S (1-Naphthol-3,8-disulphonic Acid)** ( $\text{C}_{10}\text{H}_5(\text{OH})(\text{SO}_3\text{H})_2$ ) — An intermediate for dyestuffs.

**ACID, BADISCHE (2-Naphthylamine-8-sulphonic Acid)** ( $\text{C}_{10}\text{H}_6(\text{NH}_2)(\text{SO}_3\text{H})$ ) — An intermediate for dyestuffs.

**ACID, BAYER'S (2-Naphthol-8-sulphonic Acid)** ( $\text{C}_{10}\text{H}_6(\text{OH})(\text{SO}_3\text{H})$ ) — An intermediate for dyestuffs.

**ACID, BRÖNNER'S (2-Naphthylamine-6-sulphonic Acid)** ( $\text{C}_{10}\text{H}_6(\text{NH}_2)(\text{SO}_3\text{H})$ ) — An intermediate for dyestuffs.

**ACID, CLEVES (1-Naphthol-5-sulphonic Acid)** ( $\text{C}_{10}\text{H}_6(\text{OH})(\text{SO}_3\text{H})$ )— An intermediate for dyestuffs.

**ACID, F** — Name applied to no less than six different naphthalene-sulphonic acid derivatives (amino and hydroxy) used as intermediates in the manufacture of dyestuffs.

**ACID, FREUND'S (1-Naphthylamine-3,6-disulphonic Acid)** ( $\text{C}_{10}\text{H}_5(\text{NH}_2)(\text{SO}_3\text{H})_2$ ) — An intermediate for dyestuffs.

**ACID, G (2-Naphthol-6,8-disulphonic Acid)** ( $\text{C}_{10}\text{H}_5(\text{OH})(\text{SO}_3\text{H})_2$ ) — An intermediate for dyestuffs.

**ACID, GAMMA (2-Amino-8-naphthol-6-sulphonic Acid)** ( $\text{C}_{10}\text{H}_5(\text{NH}_2)(\text{OH})(\text{SO}_3\text{H})$ ) — An intermediate for dyestuffs.

**ACID, H (1-Amino-8-naphthol-3,6-disulphonic Acid)** ( $\text{C}_{10}\text{H}_4(\text{OH})(\text{NH}_2)(\text{SO}_3\text{H})_2$ ) — An intermediate for dyestuffs.

**ACID, J (2-Amino-5-naphthol-7-sulphonic Acid)** ( $\text{C}_{10}\text{H}_5(\text{NH}_2)(\text{OH})(\text{SO}_3\text{H})$ ) — An intermediate for dyestuffs.

**ACID, K (1-Amino-8-naphthol-4,6-disulphonic Acid)** ( $\text{C}_{10}\text{H}_4(\text{NH}_2)(\text{OH})(\text{SO}_3\text{H})_2$ ) — An intermediate for dyestuffs.

**ACID, KOCH'S (1-Naphthylamine-3,6,8-trisulphonic Acid)** ( $\text{C}_{10}\text{H}_4(\text{NH}_2)(\text{SO}_3\text{H})_3$ ) — An intermediate for dyestuffs.

**ACID, L (1-Naphthol-5-sulphonic Acid)** ( $C_{10}H_6(OH)(SO_3H)$ ) — An intermediate for dyestuffs.

**ACID, LAURENT'S (1-Naphthylamine-5-sulphonic Acid)** ( $C_{10}H_6(NH_2)(SO_3H)$ ) — An intermediate for dyestuffs.

**ACID, M (1-Amino-5-naphthol-7-sulphonic Acid)** ( $C_{10}H_5(NH_2)(OH)(SO_3H)$ ) — An intermediate for dyestuffs.

**ACID, NAPHTHIONIC (1-Naphthylamine-4-sulphonic Acid)** ( $C_{10}H_6(NH_2)(SO_3H)$ ) — An intermediate for dyestuffs.

**ACID, NEVILLE AND WINTHER'S (1-Naphthol-4-sulphonic Acid)** ( $C_{10}H_6(OH)(SO_3H)$ ) — An intermediate for dyestuffs.

**ACID, PERI (1-Naphthylamine-8-sulphonic Acid)** ( $C_{10}H_6(NH_2)(SO_3H)$ ) — An intermediate for dyestuffs.

**ACID PUMPS** — See Pumps.

**ACID, R (2-Naphthol-3,6-disulphonic Acid)** ( $C_{10}H_5(OH)(SO_3H)_2$ ) — An intermediate for dyestuffs.

**ACID, 2R (2-Naphthol-3,6-disulphonic Acid)** ( $C_{10}H_5(OH)(SO_3H)_2$ ) — An intermediate for dyestuffs.

**ACID RESISTANCE** — See Bricks, Cements, Chemical Plant, Corrosion, Iron, and Refractories.

**ACID, S (1-Naphthylamine-4,8-disulphonic Acid)** ( $C_{10}H_5(NH_2)(SO_3H)_2$ ) — An intermediate for dyestuffs.

**ACID, SCHÄFFER'S (2-Naphthol-6-sulphonic Acid)** ( $C_{10}H_6(OH)(SO_3H)$ ) — An intermediate for dyestuffs.

**ACID, SULPHANILIC** ( $C_6H_4(NH_2)SO_3H$ ) (1,3) — An intermediate for dyestuffs.

**ACID, TOBIAS' (2-Naphthylamine-1-sulphonic Acid)** ( $C_{10}H_6(NH_2)(SO_3H)$ ) — An intermediate for dyestuffs.

**ACID VALUE** — See Fats.

**ACIDIMETRY** — The determination of amount of acid in a solution by titration with a standard alkali solution. (See Analytical Chemistry.)

**"ACIDOL"** — A pharmaceutical preparation of betaine hydrochloride, a colourless crystalline substance which upon solution in water hydrolyses, yielding hydrochloric acid. It is used therapeutically, and is a potential source of various methyl amines. (See Betaine.)

**ACIDS AND BASES** — In early times certain volatile materials, such as spirit of vinegar or oil of vitriol were known to change the colour of vegetable dyes, to taste sour, and to act on various metals, earths, and alkalis when properly diluted with water. In these reactions their sour or acid principles were neutralized. Often it could be shown that the product was a "neutral salt" and was a soluble, crystalline substance with a characteristic taste, such as sea salt. For example: not only  $HCl$  and  $H_2SO_4$ , but also  $SO_3$ ,  $SO_2$ ,  $CO_2$ , and  $Cl_2$  were considered to be acids since their aqueous solutions had a sour taste, acted on vegetable dyes, and on metals, earths, and alkalis to yield salt-like products.

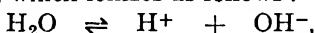
Boyle listed the properties of acids as follows: "They dissolve many substances, they precipitate sulphur from its solution in alkalis, they

change blue plant dyes to red, they lose all these properties in contact with alkalis." It should be noted that the substance itself was called an acid if it had the above characteristics.

The "base" of a salt was considered as the non-volatile residue when a salt yielded up its spirit or "acid" on distillation. Thus when copper sulphate,  $\text{CuSO}_4$ , was distilled it gave up its volatile acid,  $\text{SO}_3$ , and left behind its non-volatile residue base,  $\text{CuO}$ .

An attempt to interpret the above accurate descriptions of acids and bases led to certain partial misconceptions, for example, the oxygen acidifying principle of Lavoisier, and the common concept of the hydrogen theory of acids employed by Sir Humphry Davy and later by Arrhenius. This latter concept is widespread and is partly satisfactory when water solutions are considered. Thus the familiar definitions: "An acid is a hydrogen compound which in water solution gives hydrogen ion, a base is a hydroxyl compound which in water solution gives hydroxyl ion." By this definition  $\text{CH}_4$ ,  $\text{SO}_3$ , and  $\text{SnCl}_4$  are not acids, and  $\text{K}_2\text{O}$ ,  $\text{NH}_3$ , and  $\text{C}_2\text{H}_5\text{OH}$  are not bases.

Acidity and alkalinity when restricted to water solutions refer to an unbalance in the concentration of the solvent ions by the solute. In the case of water, which ionizes as follows:

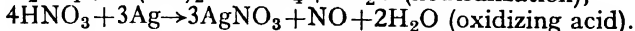
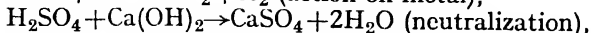
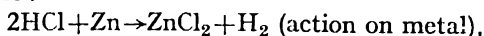


we have the fundamental elements for the acid principle and the base principle. When hydrogen chloride is dissolved in water forming hydrochloric acid there is an unbalance in the ratio of  $\text{H}^+$  to  $\text{OH}^-$  greatly in favour of the hydrogen ion yielding an acid solution. When sodium hydroxide is dissolved in water the ratio of  $\text{OH}^-$  to  $\text{H}^+$  is greatly increased and a base solution results.

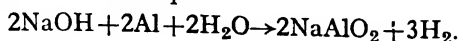
It should be noted that in this concept neither hydrochloric acid dissolved in toluene, nor pure hydrogen sulphate is acidic; neither fused potassium hydroxide nor liquid ammonia solution of sodium amide is basic.

Under this hydrogen-ion theory of acids and bases:

(1) An acid has the following properties: Turns blue litmus red, neutralizes bases to form salts and water, a non-oxidizing acid reacts with metals above hydrogen in the activity series to liberate hydrogen and form a salt, an oxidizing acid reacts with metals above or below hydrogen in the activity series but pure hydrogen is not liberated, a water solution conducts the electric current and has a sour taste. For example:



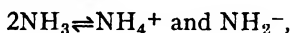
(2) A base has the following properties: A water soluble base turns red litmus blue, neutralizes acids to form salts and water, conducts the electric current, and has a bitter taste. Solutions of sodium or potassium hydroxide react with certain metals like aluminium and zinc to liberate hydrogen. For example:



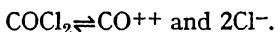
On the above basis acids and bases in water solution have various strengths depending on their degree of dissociation (ionization) as determined by measuring the electrical conductivity of various acids or bases of equivalent concentration. Illustration: Strong acids: hydrochloric acid, sulphuric acid, nitric acid. Weak acids: acetic acid, carbonic acid.

These concepts are clear and self-consistent and are probably adequate when used within the limitations imposed by the definitions. They have, however, been attacked from various points of view. How can they explain the blast furnace concept of acid ores and basic ores, acidity in the petroleum industry, and the organic and inorganic non-aqueous acidic and basic systems?

There has been an attempt to work out for every solvent an acid-base system similar to the common one used for water. Thus in liquid ammonia the system would be:



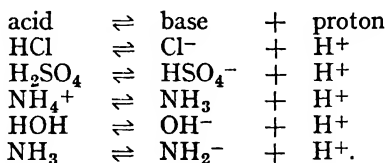
and for phosgene:



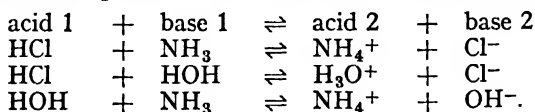
For general use these systems have not been developed into practical working mechanisms.

In 1923 T. M. Lowry in England and J. N. Brønsted in Denmark proposed a novel set of definitions that has had considerable success among workers in reaction mechanisms and kinetics. The fundamental concepts of this theory are based upon consideration of acids and bases as differing in behaviour from salts (*i.e.*, electrolytes). Salts in this theory are considered as assemblages of ions whose essential behaviour is described by the interionic attraction theory of Debye, Onsager, and others. Acids and bases, on the other hand, are uniquely characterized by a tendency to exchange protons by the fundamental reaction equation:  $\text{acid} \rightleftharpoons \text{base} + \text{proton}$ , where a proton is a hydrogen nucleus ( $\text{H}^+$ ), an acid is a proton donor, and a base is a proton acceptor.

It is inferred that an acid must be a hydrogen compound but a base is non-restricted and may in principle be any substance whatever. Thus:



Because of the nature of the proton the reactions indicated above can occur only if a proton acceptor (base) is available to compete with the original acid for its proton. The real acid-base systems are:



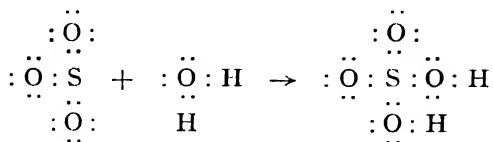
Such reactions always go spontaneously in the direction of the formation of the weaker acid and base.

Some salient features of this theory are: acid-base behaviour is independent of any solvent but includes all protolytic solvents; ions are given the status of acids and bases equivalent to that of uncharged molecules; the concept of neutrality loses its meaning since an acid and a base react to form a new acid and base;  $\text{HCl}(\text{H}_2\text{O})$  and  $\text{NH}_4\text{Cl}$  are not themselves acids but salts which contain the acids  $\text{H}_3\text{O}^+$  and  $\text{NH}_4^+$  respectively;  $\text{KOH}$  and  $\text{NaNH}_2$  are not bases but contain the  $\text{OH}^-$  and  $\text{NH}_2^-$ , respectively;  $\text{SO}_3$ ,  $\text{BCl}_3$ ,  $\text{CO}_2$  are excluded from being acids for lack of hydrogen; the fact that a substance is an acid in one set of circumstances does not prevent it from being an active base under another set ( $\text{H}_2\text{CN}^+$  is an acid formed from  $\text{H}^+$  and  $\text{HCN}$ ).

None of the hydrogen theories of acids explain the acidic properties of  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{SiO}_2$ , and others, that would come under the description of the early workers and of Boyle. G. N. Lewis says: "To restrict the group of acids to those substances which contain hydrogen interferes as seriously with the systematic understanding of chemistry as would the restriction of the term oxidizing agent to substances containing oxygen." Berzelius who considered all oxides of non-metals as acids and oxides of metals as bases was also the first proponent of the dualistic electrochemical view which Lewis, Germann, and Usanovich have developed under the titles of "The electron-pair system" and "The positive-negative system."

The electron-pair system of acids and bases was first put forward by G. N. Lewis in 1923. In this concept an acid is defined as a particle, neutral or charged, which accepts a pair of electrons from another particle in order to complete its normal octet electron grouping. A base acts as a donor of a pair of electrons to an ion or a molecule.

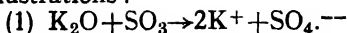
This concept of protonic solvents is essentially the same as the Brønsted-Lowry concept, but has the advantage of taking in non-protonic solvents. Consider the following:



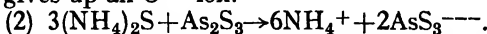
The sulphur atom in the sulphur trioxide (an acid) is capable of accepting a share in an electron pair from water (a base) to form a co-ordinate bonded compound, namely, sulphuric acid.

The positive-negative system, proposed by Usanovich in 1939, extends the above idea to oxidizing and reducing agents. Both acids and oxidizing agents, he claims, are electron acceptors, and contrariwise bases and reducing agents are electron donors. An acid accepts a share of an electron pair with a base, whereas an oxidizing agent takes over completely the electron or electrons donated by a reducing agent. Depending upon the conditions, a substance may possibly act as an acid or a base or an oxidizing agent or a reducing agent.

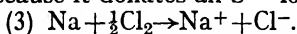
Illustrations :



$\text{SO}_3$  is an acid because it takes up an  $\text{O}^{--}$  ion, and  $\text{K}_2\text{O}$  is a base because it gives up an  $\text{O}^{--}$  ion.



$\text{As}_2\text{S}_3$  is an acid because it accepts an  $\text{S}^{--}$  ion, and  $(\text{NH}_4)_2\text{S}$  is a base because it donates an  $\text{S}^{--}$  ion.



$\frac{1}{2}\text{Cl}_2$  is an acid because it accepts an electron, and Na is a base because it donates an electron.

The common bases or alkalis include the oxides of potassium and sodium, their hydroxides and carbonates; ammonia and ammonium carbonate; the alkaline earths and their carbonates; and many organic bases, of which the amines and the alkaloids are representative.

The following compounds are all more or less basic in character: the hydrides of phosphorus, antimony, and arsenic, and their alkyl substituted derivatives.

$\text{PH}_3$ , phosphine

$\text{P}(\text{CH}_3)_3$ , trimethyl phosphine

$\text{AsH}_3$ , arsine

$\text{As}(\text{C}_2\text{H}_5)_3$ , triethyl arsine

$\text{SbH}_3$ , stibine

$\text{Sb}(\text{CH}_3)_3$ , trimethyl stibine

*References: Acids and Bases, A Collection of Papers* (Journal of Chemical Education, Easton, Penn.); *More Acids and Bases, A Collection of Papers* (Journal of Chemical Education, Easton, Penn.); *Salts, Acids and Bases*, by Walden (McGraw-Hill Book Co., New York); *The A.B.C. of Acid-Base Chemistry*, by Horace W. Davenport (University of Chicago Press); "Acids and Bases," by G. N. Lewis (*J. Franklin Inst.*, **226**, 293 (1938)); "Theory of Acids and Bases," by M. Usanovich (*J. Gen. Chem.*, U.S.S.R., **9**, 182 (1939)); "The Electronic Theory of Acids and Bases," by W. F. Luder (*Chem. Rev.*, **27**, 547 (1940)); and pH Value.

**Organic Acids** are of immense numbers and diverse characters, as shown by the following selected list of those containing only the elements carbon, hydrogen, and oxygen (the carboxylic acids) (others contain the elements nitrogen or sulphur with carbon):

#### SELECTED LIST OF CARBOXYLIC ACIDS

NAME OF ACID	FORMULA	MELTING POINT, °C	BOILING POINT, °C	SPECIFIC GRAVITY, AT 20 °C
Carbonic .. ..	$(\text{HO})_2\text{CO}$			
Formic .. ..	$\text{H.COOH}$	8.6	100.8	1.220
Acetic .. ..	$\text{CH}_3\text{COOH}$	16.7	118	1.049
Propionic .. ..	$\text{C}_2\text{H}_5\text{COOH}$	-22	141	0.992
Butyric .. ..	$\text{C}_3\text{H}_7\text{COOH}$	-4.7	164	0.959
Valeric .. ..	$\text{C}_4\text{H}_9\text{COOH}$	-35	187	0.942
Caproic .. ..	$\text{C}_5\text{H}_{11}\text{COOH}$	-1.5	202	0.922
Heptylic .. ..	$\text{C}_6\text{H}_{13}\text{COOH}$	-10	223	0.918
Caprylic .. ..	$\text{C}_7\text{H}_{15}\text{COOH}$	16	237	0.910
Pelargonic .. ..	$\text{C}_8\text{H}_{17}\text{COOH}$	12.5	253	0.906
Capric .. ..	$\text{C}_9\text{H}_{19}\text{COOH}$	31.5	268	0.89 at 37° C.
Undecylic .. ..	$\text{C}_{10}\text{H}_{21}\text{COOH}$	29	228 at 160 mm.	
Lauric .. ..	$\text{C}_{11}\text{H}_{23}\text{COOH}$	47	225 at 110 mm.	
Tridecylic .. ..	$\text{C}_{12}\text{H}_{25}\text{COOH}$	51	236 at 100 mm.	
Myristic .. ..	$\text{C}_{13}\text{H}_{27}\text{COOH}$	57	250 at 100 mm.	

Selected List of Carboxylic Acids—*continued*.

NAME OF ACID	FORMULA	MELTING POINT, °C	BOILING POINT, °C	SPECIFIC GRAVITY, AT 20 °C
Pentadecylic ..	$C_{15}H_{31}COOH$	54	257 at 100 mm.	
Palmitic ..	$C_{16}H_{33}COOH$	63	271 at 100 mm.	
Margaric ..	$C_{18}H_{35}COOH$	60	227 at 100 mm.	
Stearic ..	$C_{17}H_{35}COOH$	69	291 at 100 mm.	
Arachidic ..	$C_{20}H_{39}COOH$	77	328 (decom.)	
Eicosanic ..	$C_{21}H_{41}COOH$	84	306 at 60 mm.	
Melissic ..	$C_{25}H_{51}COOH$	90		
Acrylic ..	$CH_2 : CH.COOH$	12.5	141	1.062
Methylacrylic ..	$CH_3 : C(CH_3)COOH$	16	162	
Crotonic ..	$CH_3CH : CHCOOH$	72	189	
Maleic (cis) ..	$COOHCH : CHCOOH$	130	135 (decom.)	
Fumaric (trans) ..	$COOHCH : CHCOOH$	286	290	
Oleic ..	$C_{17}H_{33}COOH$	14	285 at 100 mm.	0.895
Linoleic ..	$C_{17}H_{31}COOH$	< -18	230 at 16 mm.	0.903
Linolenic ..	$C_{17}H_{29}COOH$		230 at 16 mm.	0.914
Benzoic ..	$C_6H_5.COOH$	122	249	
Toluic, ortho ..	$C_6H_4(CH_3)COOH(I, 2)$	104	259	
" meta ..	" (I, 3)	110	263	
" para ..	" (I, 4)	179	274	
Phenylacetic ..	$C_6H_5.CH_2.COOH$	77	265	
Diphenylacetic ..	$(C_6H_5)_2CHCOOH$	148		
Triphenylacetic ..	$(C_6H_5)_3CCOOH$	265		
Cinnamic ..	$C_6H_5CH : CH.COOH$ , cis-	68	125 at 20 mm	
" ..	" trans-	133	300	
" ..	" iso-	58	256 (decom.)	
Oxalic ..	$COOH.COOH$	101.5		
Malonic ..	$COOH.CH_2.COOH$	130 (decom.)		
Succinic ..	$COOH(CH_2)_2COOH$	190		
Glutaric ..	$COOH(CH_2)_3COOH$	97.5	200 at 20 mm.	
Adipic ..	$COOH(CH_2)_4COOH$	152	265 at 100 mm.	
Pimelic ..	$COOH(CH_2)_5COOH$	104	272 at 100 mm.	
Suberic ..	$COOH(CH_2)_6COOH$	±142	279 at 100 mm.	
Azelaic ..	$COOH(CH_2)_7COOH$	106	286 at 100 mm.	
Sebacic ..	$COOH(CH_2)_8COOH$	134	294 at 100 mm.	
Glycolic ..	$CH_2OH.COOH$	79		
Lactic ..	$CH_3.CHOH.COOH$	d- or l- 53		
Malic ..	$COOH.CH_2.CHOH.COOH$	dl- 18	122 at 14 mm.	1.249
Tartaric ..	$COOH(CHOH)_2COOH$	d- or l- 99	150 (decom.)	
		dl- 128		
		168-170		
		meso(i-)		
		140		
		racem. (dl-)		
Gluconic ..	$CH_2OH(CHOH)_4COOH$	205		
Mucic ..	$COOH(CHOH)_4COOH$	125		
Saccharic ..	$COOH(CHOH)_4COOH$	204-214 (decom.)		
Citric ..	$COOH.CH_2.C(OH)(COOH).$	125		
Salicylic ..	$C_6H_4(OH)(COOH)(I, 2)$	153		
Hydroxybenzoic ..	$C_6H_4(OH)(COOH)(I, 3)$	159		
" ..	" (I, 4)	201		
		213		

The phenols and cresols, or so-called tar acids, while having weak acid-like characters, stand in a class by themselves and to some extent behave like alcohols.

*References: Fatty Acids and Their Derivatives*, by A. W. Ralston (John Wiley and Sons, New York); *Fatty Acids. Their Chemistry and Physical Properties* (Interscience Publishers, New York).

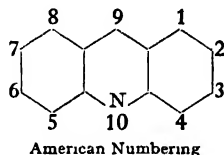
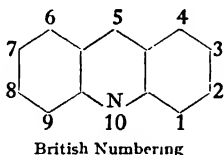
**ACONITIC ACID** ( $\text{COOH}.\text{CH}:\text{C}(\text{COOH}).\text{CH}_2.\text{COOH}$ ) — A crystalline substance of m.p.  $191^\circ\text{C}$ ., soluble in water, occurring naturally in the root of *Aconitum napellus* (a perennial herb found in the lower mountain slopes of Central Europe and cultivated in England), shave-grass, and cane-juice. It is tribasic and can be prepared by the careful dehydration of citric acid.

**ACONITINE** ( $\text{C}_{34}\text{H}_{47}\text{O}_{11}\text{N}$ ) — A white, crystalline, extremely poisonous alkaloid of m.p.  $204^\circ\text{C}$ . obtained from aconite root; soluble in alcohol and ether. The root of *Aconitum napellus* (Monkshood) contains from 0.2 to 1.5 per cent. of the alkaloid associated with several others, the chief of which are picraconitine and aconine. Aconite is used medicinally, mainly in liniments as a local analgesic. (See *Plant Alkaloids*, by Henry (1939), and historical review in *Amer. Pharm. Ass. Monog.*, No. 1 (1938).) Some Indian aconites contain an alkaloid named pseudoaconitine ( $\text{C}_{36}\text{H}_{51}\text{O}_{12}\text{N}$ ), of m.p.  $212^\circ\text{C}$ . (See T. M. Sharp, *J.C.S.*, 1928, 3094.)

**ACRAMINE RED** ( $\text{C}_{13}\text{H}_{11}\text{N}_3.\text{HCl}$ ) — A red dye, namely, 3,7-diaminoacridine hydrochloride. It is used in medicine as an antiseptic and is stated to be the least toxic and least irritant of the acridine dyes.

**ACRAMINE YELLOW** — See Aminacrine Hydrochloride.

**ACRIDINE** ( $\text{C}_{13}\text{H}_9\text{N}$ )



A heterocyclic base occurring in heavy tar oils. A colourless crystalline irritating substance and the parent of important pharmaceuticals. (See Acriflavine, and Mepacrine.)

**ACRIFLAVINE** — An orange-red dye, consisting of a mixture of the hydrochlorides of 3,6-diamino-10-methylacridinium chloride and 3,6-diaminoacridine; soluble in water and alcohol. Used in medicine as an antiseptic.

**ACROLEIN** ( $\text{CH}_2:\text{CH}.\text{CHO}$ ) — A substance of aldehydic character produced by the oxidation of allyl alcohol ( $\text{CH}_2:\text{CH}.\text{CH}_2.\text{OH}$ ), and by the destructive decomposition of fats by heat. It is a colourless, inflammable, and poisonous liquid of extremely pungent odour, having a violent action on the eyes. Sp. gr. 0.84; b.p.  $52^\circ\text{C}$ .: soluble in water, alcohol and ether. It yields acrylic acid ( $\text{CH}_2:\text{CH}.\text{COOH}$ ) by oxidation, and this, upon fusion with alkali, breaks up into acetic and formic acids. See *Newer Methods of Preparative Organic Chemistry* (Interscience Publishers, New York).

“**ACROLITE**” — A synthetic resin made by condensation from glycerol and phenol.

**ACRYLIC ACID** — See Acrolein.

**"ACRYLOID "** (*Acrylic Resins*) — Polymers of acrylates and methacrylates, distinguishable from other resins by their colourless transparency, high elasticity, resistance to many reagents, and adhesive qualities. They are optically clear, of high light transmission, of density 1.8, and permanently thermoplastic. They are used as intermediate layer in laminated glass, under the names of "Luglas" and "Sigla" in Europe and "Plexite" in the United States. These resins are in general insoluble in water, in alcohols, and in paraffin hydrocarbons, but form solutions or gels in coal-tar hydrocarbons, in chlorinated hydrocarbons, in esters, in ketones, in ether alcohols, and in ether esters, which solutions are used for lacquer coatings on metal, wood, textiles, and paper, either by brushing or spraying. See L. Klein and W. T. Pearce on "Polymerized Acrylic Acid Derivatives" (*Ind. Eng. Chem.*, 28, 635 (1936)).

**"ACTICARBONE "** — See Carbon.

**ACTINIUM** — Element 89, symbol Ac, the longest lived isotope is of mass 227 and this is given as the atomic weight. Discovered independently by A. Debierne in 1899 and F. Giesel in 1902.

**ACTINOMETERS** — Instruments for measuring photochemical intensity of light, as exhibited by exposure of chemical substances thereto.

**ACTIVATION** — The activity of certain substances may be increased by a treatment such as exposure to heat, to light, or by the presence of another substance. The process of preparation is called activation, and the resulting substance is said to be activated. A substance added to another to produce such a result is called an activator or promoter. See Aluminum, activated alumina; Carbon, activated; Colloid Chemistry; Nitrogen Fixation; Silicon, silica "gel."

**ACYCLIC** — A term descriptive of open-chain carbon compounds such as the olefines and paraffins. (See Cyclic.)

**ACYL RADICALS** — The radicals left after removal of OH from organic acids—for example,  $\text{CH}_3\text{CO}$  (acetyl),  $\text{C}_2\text{H}_5\text{CO}$  (propionyl) derived respectively from acetic and propionic acids.

**"ADALIN "** — See Carbromal.

**ADDITION COMPOUNDS** are those formed, as it were, by mere addition of elements to compounds or by molecular combination instead of by substitution or replacement. For example, ethylene ( $\text{C}_2\text{H}_4$ ), an unsaturated hydrocarbon, combines with chlorine, forming ethylene chloride ( $\text{C}_2\text{H}_4\text{Cl}_2$ ), by direct addition, thus satisfying two spare affinities of the carbon atoms in the ethylene.

An additive reaction is one in which two or more molecules react to yield one product; similarly the direct combination of sulphur and oxygen forming sulphur dioxide is an additive reaction.

**ADENINE** ( $\text{C}_5\text{H}_5\text{N}_5 \cdot 3\text{H}_2\text{O}$ ) — A nuclein base, 6-aminopurine, found in the pancreas and in a number of vegetable growths including lucerne. Physiologically important as occurring in combination in the nucleoproteins and the co-enzymes. (See Nucleins.)

**ADEPS LANÆ (Anhydrous Lanolin)** — A refined wool fat of m.p. about 40° C., containing cholesterol, isocholesterol, and various esters, prepared from "suint." From investigations made at the National Physical Laboratory at Teddington, lanolin brushed on or deposited from a solution would appear to be the best coating as a preservative for the bright steel parts of stored machinery; solvent naphtha and white spirit proving the best carriers. (See Special Report No. 12 of the Engineering Research Board, H.M. Stationery Office). It is also used for super-fatting toilet soaps and in preparing ointments and cosmetics. (See Wool.)

**ADEPS LANÆ HYDROSUS (Lanolin)** — Wool fat containing 30 per cent. water, used medicinally as an emollient.

**ADHESIVES** — Some varieties are made from the proteins or alkali-proteins which are isolated from the residues resulting from the extraction or expression of oils from seeds, and in particular hemp-seed and castor-beans. These are treated with suitable bases, such as the alkaline-earth hydroxides or magnesia, and with an alkali salt, such as sodium fluoride or arsenate, the resulting product being then mixed with dilute alkali hydroxide solution.

Among other proteins the casein precipitated from skimmed milk by the action of rennet or acids is used, being passed through a 60-mesh sieve after washing and drying. A cement having good keeping and adhesive characters, used in aeronautical construction, is made from the formula :

Casein	..	..	..	..	..	78.0 per cent.
Sodium carbonate	..	..	..	..	4.5	„
Sodium fluoride	..	..	..	..	4.0	„
Freshly slaked lime	..	..	..	..	12.5	„
Sodium arsenate	..	..	..	..	1.0	„

the ingredients being ground to pass through a 90-mesh sieve. Casein cements possess certain advantages over gelatine glues, as they keep well, are easily rendered fluid, can be used cold, and are inodorous. A cold adhesive of excellent quality is stated to be made by mixing 100 parts of an organic colloid such as casein with 10 parts alum and 3 to 5 parts of soda-ash, the whole being subsequently well mixed with 500 parts water.

Sodium silicate in solution is largely used as an adhesive, being fire-resisting and repellent to vermin.

Magnesium oxychloride mixed with 10 per cent. of finely divided copper powder is proposed by D. S. Hubbell (*Ind. Eng. Chem.*, **29**, 123 (1937)) as an inorganic adhesive and cement, which also gives a permanent bond to Portland cement.

Adhesives are also made from seaweeds, various starches, flax residue, blood albumin, rubber, citrus fruits, and gelatinous bodies such as Iceland moss, isinglass, gums, and glues, as also from the sulphite wash liquors resulting from paper-making, and from soy-bean residue after extraction of the oil, and several synthetic resins or plastics.

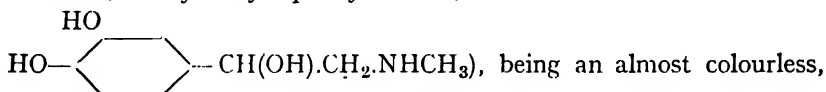
Adhesives are used in the manufacture of plastic materials, distempers, ply-wood, briquettes, and many other industries.

See "Rubber Cements and Adhesives," by S. D. Sutton (*Ind. Chem.*, **8**, 65 (1932)); *Principles of High Polymer Theory and Practice*, by A. X. Smith and C. A. Marlies (McGraw-Hill Book Co., New York); *Technology of Adhesives*, by John Delmonte (Reinhold Publishing Corp., New York); Agar-Agar, Algin, "Arboneeld," Bones, Briquetting, Cement, "Elvacet," "Elvaol," Gelatine, Glue, Gums, Isinglass, Mucilage, Neoprene, and Size.

**ADIPIC ACID** ( $C_4H_8(COOH)_2$ ) — A member of the oxalic series of acids, a constituent of beet juice, and produced by the action of nitric acid upon oleic acid and other fatty acids or on cyclohexanone, which is the source for nylon. It is a solid crystalline body soluble in alcohol, ether, and hot water, of m.p.  $152^\circ C$ . It is stated to be superior to tartaric acid for use in making baking powder, salines, and fruit essences. Used also in the manufacture of plasticizers and nylon. (See Nylon.)

**ADIPOSE (Substance)** — Animal oil or fat.

**ADRENALINE (Epinephrine)** ( $C_9H_{13}O_3N$ ) — A hormone (*l*-2-methyl-amino-3',4'-dihydroxy-1-phenylethanol,



being an almost colourless, crystalline base, of m.p.  $205^\circ$  to  $212^\circ C$ ., and constituting the active principle of the suprarenal gland. It is prepared from an acid extract of the suprarenal glands of sheep and cattle or by synthesis. It is slightly soluble in water but insoluble in alcohol, ether, and chloroform. The hydrochloride, or preferably the tartrate, is used in medicine as a hæmostatic and vasoconstrictor. When injected into the circulation, it increases the blood pressure by constricting the vessels, reduces the peristaltic movements of the gut and is said to produce "all the vascular and visceral reactions which accompany the emotions of anger, excitement, and fright." The *l*-isomer is more physiologically active than the *d*-isomer. The racemic compound, suprarenine, obtained synthetically from pyrocatechol, is less powerful in physiological action than the naturally occurring lævo-rotatory form. (See Cori and Welch in *J. Am. Med. Ass.*, **116**, 2590 (1941); J. D. P. Graham in *J. Pharm. et Pharmacol.*, **1**, 17 (1949); H. Barcroft and H. Konzett in *Lancet*, **256**, 147 (1949); and Z. M. Bacq in *J. Pharmacol.*, **95**, 1 (1949).)

The presence of *nor*-adrenaline in biological material and in crystalline adrenaline derived from adrenal glands has been demonstrated. (See B. F. Tullar, *Scienc*, **109**, 536 (1949); Auerbach and Angell, *ibid.*, **109**, 537 (1949); P. Holton, *Nature* (London), **163**, 217 (1949); von Euler and Hamberg, *ibid.*, **163**, 642 (1949); Bulbring and Burn, *Brit. J. Pharmacol.*, **4**, 202 (1949); Burn and Hutcheon, *ibid.*, **4**, 373 (1949); and Gladdum and Lembeck, *ibid.*, **4**, 401 (1949).)

**ADSORPTION** refers to the existence of a higher concentration of a component at the surface of a phase than is present in the main bulk of the phase. For example, charcoal, silica, and alumina can and do adsorb large quantities of gases upon their surfaces. This phenomenon is utilized in removing odours, colours, and moisture from various systems. (See Carbon, Silica.)

The surface of a liquid is under strain due to unbalanced van der Waals forces on the surface molecules. This strain gives rise to the phenomenon known as surface tension or capillary action of liquids. A solid is also subjected to internal forces which are unbalanced at the surface of the solid thus making it possible for the solid surface to attract foreign material. This tendency causes the concentration of the foreign material to be greater at the surface of the solid than at any place in the immediate vicinity. Adsorption is the result of these unbalanced surface forces acting on material that comes into their field of influence.

It is very likely that adsorption occurs on all surfaces but since large objects have a relatively small area to mass ratio the phenomenon is not very noticeable. If, however, a large particle is subdivided many times, to the dimensions of the colloidal state, the area to mass ratio will be very large (see Colloidal State) and adsorption becomes a very important factor in the behaviour of the system.

The amount of adsorption that a given substance will show toward a gas is related to the surface area, the temperature and the pressure in the following manner: The amount of the adsorption is directly related to the surface area and pressure and inversely related to the temperature. Over limited ranges of pressure, at constant temperature, the Freundlich adsorption isotherm,  $\frac{x}{m} = kP^{\frac{1}{n}}$ , is valid, where

$x$  is the mass of gas adsorbed by  $m$  grams of material at the pressure  $P$ , and  $n$  and  $k$  are constants for a given system at a given temperature.

Two fundamental types of adsorption are recognized depending upon whether the association at the phase interface is physical (van der Waals forces) or chemical in character. Physical adsorption shows low heats of adsorption, complete reversibility between the two phases of the system and generally low activation energies at low temperatures. All gases exhibit physical adsorption to a greater or lesser degree.

Chemical adsorption (chemisorption), which utilizes forces of a chemical nature, often accompanies physical adsorption. Chemisorption shows higher heats of adsorption, and generally is not completely reversible. Frequently adsorption seems to be physical at low temperatures but changes to chemisorption at higher temperatures. For example, at  $-200^{\circ}\text{C}$ . nickel adsorbs large quantities of hydrogen but as the temperature rises the quantity adsorbed drops off sharply, but increases again toward a maximum value at about  $-100^{\circ}\text{C}$ ., then subsequently falls off slowly.

While adsorption is generally thought of in terms of solids and gases it should exist in all systems where interfaces appear, thus, adsorption at the surfaces of liquids and solutions is a very real thing and is

becoming increasingly important in the commercial world as is evidenced by the appearance of detergents on a large scale. On the basis of general considerations a solute that lowers the surface tension at an interface of a liquid will tend to increase the concentration of that solute in the surface over the concentration in the body of the solution. Such solutes are said to be *surface active*. Conversely, if a solute increases the surface tension it will tend to become less concentrated in the surface. This phenomenon, demonstrated by many electrolytes, is called *negative adsorption*.

The formation and utilization of unimolecular films in optics and related fields is undoubtedly a demonstration of adsorption. The ability of certain solids to adsorb colouring matter and other substances from solution is a well known fact, but the mechanism controlling the process is not so well understood. Possible explanations of this problem may be: (1) By virtue of the molecular or chemical attraction between the solid and the foreign material, (2) by virtue of providing a large surface area at which a surface active material may accumulate. Undoubtedly these two properties as well as others less clearly understood are involved. Chromatographic analysis is a direct and important application of this phenomenon.

*References*: *Textbook of Physical Chemistry*, by S. Glasstone (D. Van Nostrand Company, Inc., New York, London); "General Discussion," *Trans. Faraday Soc.*, **36** (1940); *Physical Adsorption*, by Stephen Brunauer (Princeton University Press); *Surface Chemistry*, Faraday Society Report (Interscience Publishers, New York); *Adsorption*, by C. L. Mantell (McGraw-Hill Book Co., New York).

**AERATION** — Charging of liquids with gases. So-called soda-water is water (with or without addition of a little alkali) charged with carbon dioxide gas under pressure. Water can also be charged with air or oxygen gas. Many natural sparkling waters are more or less charged with gases.

**AEROLITES** — See Metcorites.

**AEROSOLS** — Colloidal suspensions of liquids or solids in a gaseous medium. Some insecticides, particularly pyrethrum and D.D.T. have been found to be highly effective when dispersed as aerosols. Dispersion may be accomplished in several ways, one of the most common being the pressure "aerosol bomb," in which the insecticide and propellant gas are confined under pressure inside a metal cylinder. "Freon-12" is most frequently used as a propellant. The insecticide is applied by opening a valve and releasing the mixture in a finely divided form. (See "Definition of Aerosol," by R. C. Roark (*J. Econ. Entomol.*, **35**, 105 (1942)); "Insecticidal Aerosols," by L. D. Goodhue (*J. Econ. Entomol.*, **37**, 338 (1944)); "Aerosols," by F. T. Grucker, Jr. (*Scientific Monthly*, **48**, No. 6 (June, 1949)); also Colloid Chemistry, Dusts, "Freon," and Insecticides.)

**"AEROSPORIN"** — See Bacillosporin.

**ÆSCULIN** — See Glycosides.

**ETHER** — See Ether.

**AFFINITY** — See Chemical Interactions.

**AFTERGLOW** — The persistence of luminescence in an electrical discharge tube after the current has been cut off. The brief afterglow of "active" nitrogen is an example of this phenomenon.

**AGAR (Agar-Agar)** — The dried, colloidal residue obtained from a decoction of various seaweeds, notably, *Gelidium cartilagineum*, *Gelidium Amansi*, *Gracilaria confervoides* and *Hypnea musciformis* (Rhodophyceæ), produced in Japan, California, Australia, New Zealand, and Ceylon. The algæ are collected in summer and autumn but are processed later during the cold season. The seaweed is first soaked to remove sand, then extracted with hot water, filtered and cooled to form a gel. The gel is frozen, pressed to remove water, and thawed and filtered through rotary vacuum filters. The flakes of agar are finally dried by ascending currents of hot air in cylindrical stack driers. For an account of production in U.S.A., see C. K. Tseng, *Sci. Monthly*, **59**, 37 (1944). Production in Australia from *Gracilaria confervoides* is described by E. J. F. Wood, *J. Council Sci. Ind. Res.*, **15**, 295 (1942).

Agar occurs in translucent flakes or as a coarse powder, commercial varieties being known as Ceylon Agar, Macassar Agar, American Agar, Japanese Agar (Japanese Isinglass), Australian Agar, and New Zealand Agar. A 1 per cent. solution forms a firm jelly. Agar is carbohydrate in nature, consisting mainly of the calcium salt of a sulphuric ester of *d*-galactose (see Percival and Somerville, *J. Chem. Soc.*, **1937**, 1615; Jones and Peat, *J. Chem. Soc.*, **1942**, 225; and Percival and Thomson, *J. Chem. Soc.*, **1943**, 750). Japanese Agar may be distinguished microscopically by the presence in it of disc-shaped diatoms of the *Arachnoidiscus* species.

Agar is used for a variety of purposes such as the preparation of bacterial culture media, the sizing of silk, as an adhesive and as an emulsifying agent. For an account of its uses, see C. K. Tseng, *Sci. Monthly*, **58**, 24 (1944); **59**, 37 (1944). British Agar is obtained from *Chondrus Crispus* and *Gigartina stellata* and its production is described in *A Study of Certain British Seaweeds and their Utilization in the Production of Agar*, published by H.M.S.O., London, 1949.

**AGATE** — An anhydrous form of natural silica ( $\text{SiO}_2$ ) of crystal system No. 3, being a variegated *chalcodony* found in many parts of the U.S.A. and elsewhere. Some analyses of agate are given by H. Heinz (*B.C.A.*, **A**, 1930, 1016). (See Silicon.)

**AGAVE** — See Alcohol (Ethyl).

**AGEING** — A term applied to the time of storing of various materials during which the quality changes, in some cases favourably, as in the case of clays, and in other cases unfavourably, as in the case of rubber. In some cases involving textiles ageing denotes oxidation by exposure to air.

**AGGLOMERATING AGENTS** — Substances that when added to a colloid produce aggregation or flocculation of the particles, as rennet for

coagulating milk in cheese-making. See "Some Aspects of Flocculation," by J. O. Samuel (*Ind. Chem.*, 14, 138 (1938)), where soluble hydroxides, which furnish hydroxyl ion, are shown to be effective as flocculating agents for colliery effluents.

**AGRICULTURAL CHEMISTRY** — See *A Course of Practical Work in Agricultural Chemistry*, by T. B. Wort (Cambridge Univ. Press); *Official and Tentative Methods of Analysis*, by Association of Official Agricultural Chemists, Washington, D.C.; *Chemistry and Agriculture*, by J. S. Chamberlain (Chemical Foundation, Inc., New York); *Introduction to Agricultural Chemistry*, by Dutcher and Haley (John Wiley and Sons, New York); *A Source Book of Agricultural Chemistry*, by Browne (Chronica Botanica Co., Waltham, Mass.); *Agricultural Chemistry*, by N. M. Comber *et al.* (Longmans, Green and Co., London and New York); *Agricultural Chemistry*, by Donald E. H. Frear (D. Van Nostrand Co., New York); Feeding Stuffs, Fertilizers, Fungicides, Herbicides, Insecticides, Photocatalysis, and Soils.

**AIR (Atmosphere)** — Air is substantially a mixture of oxygen gas (about 21 parts) and nitrogen gas (about 79 parts), containing small quantities of other gases, also varying proportions of moisture (water) in consequence of the continuous evaporation of water from the land and water surfaces of the earth. For any given temperature, there is a maximum amount of water vapour which a given volume of air is capable of taking up or dissolving, and under these conditions it is saturated with moisture at that particular temperature. (See Hygrometers, and accompanying Psychrometric Chart.)

A cubic metre of air at 20° C. can take up 17.16 grams of water, but at 0° C. it can only hold 4.87 grams, so that, when cooled, the excess of water held in gaseous solution is deposited as mist, dew, rain, hail, or snow.

Animal life is dependent upon the oxygen content of the air. In breathing, the oxygen of the air is sucked up or absorbed in the lungs, and reacting upon the blood forms carbon dioxide, which gas is given out in the breath—the act of respiration. The inert nitrogen which is present in the air is of no direct use in sustaining life, but serves to dilute the oxygen to the concentration at which it is most desirable for the body.

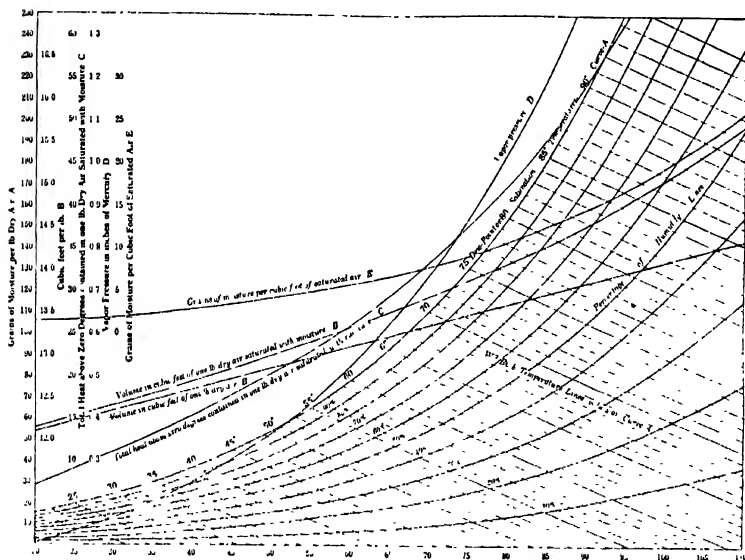
It has been estimated that the amount of carbon dioxide given off in each twenty-four hours through the lungs of an adult human being is that which results from the oxidation of between 7 and 11 ounces of carbon, and this necessitates the consumption of about 1½ pounds of oxygen gas inhaled; and if we multiply this quantity by the number of the world's inhabitants (human beings and animals) the amount of oxygen gas thus removed from the air is represented by an astounding figure. The quantity, indeed, is so large that, unless there existed some compensating process, life would in course of time become impossible on the earth. It is now known that plant life gives back to the atmosphere the oxygen which animal life removes from it. Vegetable life absorbs carbon dioxide from the air, as also from decomposing organic matter in the soil, and, assimilating the carbon in its

tissues by a variety of chemical processes, gives out again some of its oxygen content, and thus maintains the composition of the air practically constant and universal. (See Hæmatine, Photocatalysis, Respiration, and Vegetation.)

It is the oxygen of the air that sustains the combustion of fuel, the carbon (of which fuels are largely composed) entering into chemical combination therewith, forming carbon dioxide, and giving out heat at the same time.

### PSYCHROMETRIC CHART, AIR—WATER VAPOUR DATA

*Pressure of barometer, 29.92 inches of mercury  
Temperature, Fahrenheit degrees*



### DRY BULB TEMPERATURE

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Combustion is essentially dependent upon the presence of oxygen. If an ordinary candle be lighted and placed in a wide-mouthed stoppered bottle, and the bottle closed, the candle will go on burning until the oxygen contained in the air present in the bottle has been partly used up and is then extinguished; on the other hand, as is well known, it will go on burning in the open air until the candle is all consumed.

The air always contains a certain quantity of carbon dioxide—averaging 0.03 per cent. in fresh air—and this constituent is of more importance than might appear without careful consideration, bearing

in mind how essential it is to the growth and development of vegetable life, and how the quantity of oxygen contained in the air is maintained by way of compensation.

In addition to moisture and dust, the air of towns generally contains small proportions of ammonia, sulphur dioxide, hydrogen sulphide, and organic matters, whilst nitric acid is produced by lightning flashes. Appliances known as "Dust Counters" are employed for measuring atmospheric pollution by dust. At times, ozone in small proportion also forms an aerial constituent, particularly in the upper layers, and other normal constituents include argon, helium, neon, krypton, and xenon. The proportions in which these are present in air at the surface of the earth are shown below :

Argon	..	..	0.94	volume per 100 volumes of air.		
Helium	..	..	0.0004	"	"	"
Neon	..	..	0.00123	"	"	"
Krypton	..	..	0.00005	"	"	"
Xenon	..	..	0.000006	"	"	"

(See Chemical Industry Medal address by F. J. Metzger on "Traces from Tons" (*Chem. and Ind.*, 54, 209 (1935), and *Ind. Eng. Chem.*, 27, 112 (1935)); *Exploring the Upper Atmosphere*, by Dorothy Fisk (Oxford Univ. Press); *Air Pollution in Donora, Pa.*, Public Health Bulletin No. 306 (1949) (Federal Security Agency, U.S. Public Health Service, Washington, D.C.); E. W. Hewson on "Atmospheric Pollution by Heavy Industry" (*Ind. Eng. Chem.*, 36, 195 (1944)); Reports of the Advisory Committee of the Meteorological Office on Air Pollution (H.M. Stationery Office); also Oxygen, Smoke, and Water.)

The weight of a litre (1,000 c.c.) of air at 0° C. and 760 mm. of pressure is 1.2932 grams. Its density diminishes as the altitude increases and its constantly varying pressure can be registered at the earth's surface by means of the barometer. The Guggenheim Laboratory states that the temperature recorded at an elevation of 25,000 feet was 40 degrees below zero Fahrenheit in comparison with 24 degrees at the top of the laboratory where the balloon was released.

**Liquid Air** — Air is commercially liquefied by self-intensive processes depending upon the performance of internal, or both internal and external work, as in the "Linde" and "Claude" processes respectively. In the Linde process air purified from carbon dioxide and water is allowed to expand from a pressure of from 150 to 200 atm. within the coil to slightly above that of the atmospheric pressure outside the nozzle, thus realizing a liquefaction of about 5 per cent.; whereas, in the Claude process, the air is compressed to from 40 to 50 atm. and then divided into two parts, one of which is allowed to expand in a vessel to perform external work and become cool and then made to surround the other part which is sufficiently cooled to liquefy by free expansion. As oxygen is more condensable than nitrogen, the liquefied product contains a larger proportion of oxygen than ordinary air. It is a mobile liquid of slightly bluish tint, and density near that of

water, of b.p.—191° C. It can be preserved and transported over moderate distances in vacuum-walled flasks. Liquid air is so cold that when such materials as flesh or indiarubber are cooled in it they become brittle, and when struck with a hammer fly into pieces as glass does.

**AIR LIFT** — A device for continuously raising liquids to a higher level, which utilizes compressed air and has no moving parts. The air lift is fundamentally a vertical U-tube having unequal legs. Air is admitted near the bottom of the longer leg, which becomes filled with a mixture of air and liquid, while the shorter leg contains liquid only. As the air flow is increased, the density of the aerated column becomes less until it is balanced by the shorter column of pure liquid. With still more air, liquid flows down the shorter leg and up the longer leg to a higher level. In practice the downflow and upflow pipes are concentric. The depth below feed level of the air inlet (termed the submergence) should be greater than the height to which the liquid is to be raised. The efficiency of a properly designed air lift is about 70 per cent.

**AJOWAN OIL (Ptychotis Oil)** — An essential oil distilled from the fruits of *Trachyspermum Ammi*, which is cultivated in India; sp. gr. 0.910 to 0.930; ref. ind. 1.485 to 1.510 at 20° C. It contains from 40 to 55 per cent. of thymol associated with cymene and other terpenes. (See Thymol.)

**"AKLO"** — A glass having the unusual property of holding back about 70 per cent. of the heat rays and at the same time transmitting 70 per cent. of the light waves.

**"AKRITE"** — See "Stellite."

**ALABASTER** — A native form of fine-grained gypsum ( $\text{CaSO}_4$ ), used in sculpture and for ornamental applications. (See Calcium.)

**"ALATHON"** (Du Pont) — Trade-mark for a series of polyethylene (polythene) synthetic resins. Used as coating for paper to impart resistance to hot and cold water, water vapour, oils, greases, and chemicals, and is suitable for packaging foods and beverages. It can be used for heat-sealing containers.

**"ALBERTOL"** — Synthetic resins, described in the U.S.A. as "Amberol" resin, one such article being made by heating a mixture of 160 parts phenol with 40 of rosin and 40 of para-formaldehyde for 6 hours at 120° to 130° C.

**"ALBONE"** (Du Pont) — Trade-mark for hydrogen peroxide of 35 per cent. by weight. Used for bleaching vegetable and animal fibres, oils and fats, and for the production of metallic peroxides and persalts.

**"ALBUCID"** — See Sulphacetamide.

**ALBUMINATES** — Loose combinations of albumin with metals, such as the copper compound resulting from the addition of copper sulphate to a solution of albumin.

**ALBUMINOID AMMONIA** — That resulting from the decomposition of albuminous matter, serving, when determined, as indicative of the organic nitrogen content of water supplies.

**ALBUMINOIDS** — A term used in the older literature as synonymous with proteins; now used to designate a specific class of proteins which are insoluble in most solvents. Examples of albuminoids are keratin (from horn, hide, and hoofs), elastin, and collagen. (See Proteins.)

**ALBUMINOMETER (Esbach's)** — A graduated tube about 6 inches long and  $\frac{1}{2}$  inch diameter graduated so that each degree indicates 0.1 per cent. of albumin. The tube is filled to a given mark with urine, and a reagent of 1 per cent. picric acid and a 2 per cent. solution of citric acid in distilled water is then added up to another mark. This causes the precipitation of any albumin contained in the urine, and after settlement the volume is read off by the graduations on the tube.

**ALBUMINS** — One group of the so-called "simple proteins" characterized by their solubility in water. There are many naturally occurring albumins present in plant and animal tissues: typical examples are ovalbumin from egg white, lactalbumin from milk and leucosin from wheat. The albumins are readily coagulated by heat, and some of them have been obtained in crystalline form. (See *Outlines of Biochemistry*, by R. A. Gortner (John Wiley and Sons, New York); *Advances in Protein Chemistry* (Academic Press, New York); also Proteins.)

**ALBUMOSES** — See Albumins, and Proteins.

**"ALCOBRONZE"** — See Copper.

**ALCOHOL** — Without qualification, the word "alcohol" usually refers to ethyl alcohol (ethanol) ( $C_2H_5OH$ ). (See Alcohols.)

TABLE SHOWING THE SPECIFIC GRAVITIES OF VARIOUS STRENGTHS OF ETHYL ALCOHOL

Absolute Alcohol per Cent. by Volume	Absolute Alcohol per Cent. by Weight	Sp. Gr. at 15.5° C.	Absolute Alcohol per Cent. by Volume	Absolute Alcohol per Cent. by Weight	Sp. Gr. at 15.5° C.
1	0.80	.9985	55	47.29	.9242
5	4.00	.9928	60	52.60	.9134
10	8.05	.9866	65	57.24	.9020
15	12.05	.9810	70	62.50	.8899
20	16.28	.9760	75	67.93	.8772
25	20.46	.9709	80	73.59	.8637
30	24.69	.9654	85	79.80	.8494
35	28.99	.9591	90	85.75	.8337
40	33.39	.9518	95	92.40	.8159
45	39.90	.9435	100	100.00	.7939
50	42.52	.9343			

**ALCOHOL (SOLIDIFIED)** — A commercial article of this name is composed of alcohol, or alcohol and methylated spirit, with soap. One formula is—alcohol, 60 parts ; methylated spirit, 40 parts ; and sodium stearate, about 3 parts.

**ALCOHOLATES** — Analogous compounds to hydroxides ; the groups  $\text{OCH}_3$  and  $\text{OC}_2\text{H}_5$ , etc., take the place of  $\text{OH}$ —*e.g.*, sodium alcoholate ( $\text{NaOC}_2\text{H}_5$ ). Also termed alkoxides.

**ALCOHOLEMETRY** — An alcoholometer is an apparatus (resembling an ordinary graduated hydrometer) used to determine alcoholic strength of liquids.

**ALCOHOLS** — There are several classes of alcohols, all of which are characterized by their content of one or more hydroxyl groups, and described as monohydric (monatomic), dihydric, and trihydric, according to the number of these. The normal monohydric alcohols constitute a series of homologous (aliphatic) organic bodies of ascending specific gravities and boiling-points, the lower members being colourless mobile liquids, the middle ones of more oil-like character, and the higher ones solid, like paraffin in appearance and without taste or colour. Many are found in nature in combination with organic acids in oils, fats, and waxes. B. T. Brooks (*Ind. Eng. Chem.*, 27, 278 (1935)) describes the manufacture of synthetic alcohols and esters from petroleum.

**Methyl Alcohol (Methanol, Carbinol, Wood Naphtha, Wood Spirit)** ( $\text{CH}_3\text{OH}$ ) is contained in combination with salicylic acid in oil of winter-green, and is found among the products of the distillation of wood, the yield therefrom being increased by as much as 50 per cent. without lessening the production of acetic acid by adding a small amount of sodium carbonate before distillation.

A catalytic process has been devised for producing methyl alcohol from water-gas, the equation being represented as follows :  $\text{CO} + 2\text{H}_2 = \text{CH}_3\text{OH}$ . Methyl alcohol is made on a large scale by heating water-gas, or hydrogen-gas in admixture with carbon monoxide, under high pressure in presence of a suitable catalyst.

It is a limpid, colourless, volatile liquid, burns with a non-luminous flame, and is a solvent of fats, oils, aniline dyes, formaldehyde, perfumes, etc. It is soluble in water, and is used commercially in the synthesis of dyestuffs, in making formaldehyde, spirit varnishes, polishes, and the crude material is used for denaturing ethyl alcohol. Upon oxidation it yields formaldehyde ( $\text{CH}_2\text{O}$ ), and finally formic acid ( $\text{CH}_2\text{O}_2$ ). (See Methylated Spirit.)

**Ethyl Alcohol (Absolute Alcohol, Ethanol, Ordinary Alcohol, Spirits of Wine, or Grain Spirit)** ( $\text{C}_2\text{H}_5\text{OH}$ ) — Pure alcohol is a limpid, colourless, volatile, inflammable liquid. By oxidation, it is converted into acetaldehyde ( $\text{C}_2\text{H}_4\text{O}$ ), and finally acetic acid ( $\text{C}_2\text{H}_4\text{O}_2$ ). It is the product of the fermentation of sugar (glucose), and the intoxicating principle of wines, beers, and spirits (gin, whisky, brandy, and rum). The physical properties of absolute alcohol have been examined by Barbaudy and Lalancé (*B.C.A.*, A, 1930, 1356).

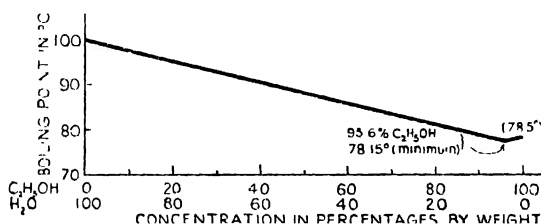
## SELECTED LIST OF ALCOHOLS

NAME	FORMULA	MELTING POINT °C.	BOILING POINT °C.	SPECIFIC GRAVITY AT 20° C.
Methyl alcohol .. Methanol	$\text{H} \cdot \text{CH}_2\text{OH}$	-98	64.7	0.792
Ethyl alcohol .. Ethanol	$\text{CH}_3 \cdot \text{CH}_2\text{OH}$	-112	78.5	0.798
95-6% plus 4-4% water .. ..			78.15	0.802
n-Propyl alcohol .. Propanol-1	$\text{C}_3\text{H}_7 \cdot \text{CH}_2\text{OH}$	-127	98	0.804
iso-Propyl alcohol .. } Propanol-2	$(\text{CH}_3)_2\text{CHOH}$	-86	82.5	0.789
Dimethyl carbinol .. }				
n-Butyl alcohol .. Butanol-1	$\text{C}_4\text{H}_9 \cdot \text{CH}_2\text{OH}$	-90	118	0.810
Methylethyl carbinol .. Butanol-2	$(\text{CH}_3)(\text{C}_2\text{H}_5)\text{CHOH}$	-115	99.5	0.808
n-iso-Butyl alcohol .. 2-Methylpropanol-1	$(\text{CH}_3)_2\text{CH} \cdot \text{CH}_2\text{OH}$	-108	107	0.805
Trimethyl carbinol .. } 2-Methylpropanol-2	$(\text{CH}_3)_3\text{COH}$	25	83	0.786
tert.-Butyl alcohol .. }				
n-Amyl alcohol .. Pentanol-1	$\text{C}_5\text{H}_{11} \cdot \text{CH}_2\text{OH}$	-78	138	0.817
iso-Amyl alcohol ..	$(\text{CH}_3)_2\text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$	-117	132	0.813
6 other $\text{C}_5$ -alcohols				
n-Hexyl alcohol .. Hexanol-1	$\text{C}_6\text{H}_{13} \cdot \text{CH}_2\text{OH}$	-52	155	0.820
n-Heptyl alcohol .. Heptanol-1	$\text{C}_7\text{H}_{15} \cdot \text{CH}_2\text{OH}$	-35	175	0.824
n-Octyl alcohol .. } Octanol-1	$\text{C}_8\text{H}_{17} \cdot \text{CH}_2\text{OH}$	-16	194	0.827
Caprylyl alcohol .. }				
Lauryl alcohol ..	$\text{C}_{11}\text{H}_{23} \cdot \text{CH}_2\text{OH}$	24	± 257	0.831 at 24° C.
Cetyl alcohol ..	$\text{C}_{18}\text{H}_{37} \cdot \text{CH}_2\text{OH}$	50	190 at 15 mm.	
Melissyl alcohol .. }	$\text{C}_{29}\text{H}_{59} \cdot \text{CH}_2\text{OH}$	88		
Myricyl alcohol .. }				
Allyl alcohol ..	$\text{CH}_2 : \text{CH} \cdot \text{CH}_2\text{OH}$	-129	97	0.854
Menthol ..	$\text{C}_{10}\text{H}_{19}\text{OH}$	42	212	0.890
Terpineol ..	$\text{C}_{10}\text{H}_{17}\text{OH}$	38	220	0.935
Benzyl alcohol .. }	$\text{C}_6\text{H}_5 \cdot \text{CH}_2\text{OH}$	-15	205	1.043
Phenyl carbinol .. }				
Benzhydrol .. }	$(\text{C}_6\text{H}_5)_2\text{CHOH}$	68	299	
Diphenyl carbinol .. }				
Triphenyl carbinol ..	$(\text{C}_6\text{H}_5)_3\text{COH}$	162	> 360	
Glycol ..	$\text{CH}_2\text{OH} \cdot \text{CH}_2\text{OH}$	-16	197	1.113
Propylene glycol ..	$\text{CH}_3 \cdot \text{CHOH} \cdot \text{CH}_2\text{OH}$		188	1.040
Glycerol .. }	$\text{CH}_2\text{OH} \cdot \text{CHOH} \cdot \text{CH}_2\text{OH}$	18	290	1.260
Glycerine .. }				
Erythritol ..	$\text{CH}_2\text{OH}(\text{CHOH})_2\text{CH}_2\text{OH}$	d- or l- 89 meso. (s-) 126 racem. (dl-) 72 102		
Arabitol ..	$\text{CH}_2\text{OH}(\text{CHOH})_2\text{CH}_2\text{OH}$			
Xylitol ..	$\text{CH}_2\text{OH}(\text{CHOH})_3\text{CH}_2\text{OH}$			
Mannitol ..	$\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}_2\text{OH}$			
Dulcitol ..	$\text{CH}_2\text{OH}(\text{CHOH})_5\text{CH}_2\text{OH}$			
Sorbitol ..	$\text{CH}_2\text{OH}(\text{CHOH})_6\text{CH}_2\text{OH}$			
Cholesterol (a zoösterol) ..	$\text{C}_{27}\text{H}_{45}\text{OH}$	148		
Ergosterol (a phytosterol) ..	$\text{C}_{27}\text{H}_{41}\text{OH}$	160-163		

Alcohol is prepared commercially from the starches of cereals or potatoes and from sugar and molasses by processes of fermentation. Ten tons of potatoes with a starch content of 37 cwts. will yield on average 255 gallons of alcohol, while a corresponding weight of grain yields 670 gallons. (See Fermentations.)

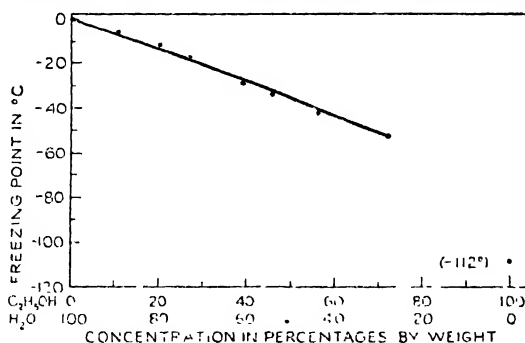
It can also be produced from the waste sulphite liquors of paper-pulp mills containing carbohydrates. The starches are first converted into maltose by the action of malt, or otherwise, the extract or "wort" being then subjected to fermentation as in brewing, and subsequently distilled in order to obtain the alcohol thus produced. (See Paper.)

ETHYL ALCOHOL ( $C_2H_5OH$ )—WATER ( $H_2O$ ) MIXTURES  
BOILING-POINT—CONCENTRATION RELATIONSHIP



Agave pulp prepared from the so-called American aloe (*Agave americana*), many species of which grow in Mexico and Central America, is used as the source of native alcoholic drinks, containing, as it does, a considerable percentage of sugar, and has been suggested as a good possible source of alcohol. The dry pulp is stated to contain up to 15 per cent. fermentable sugars.

ETHYL ALCOHOL ( $C_2H_5OH$ )—WATER ( $H_2O$ ) MIXTURES  
FREEZING-POINT—CONCENTRATION RELATIONSHIP

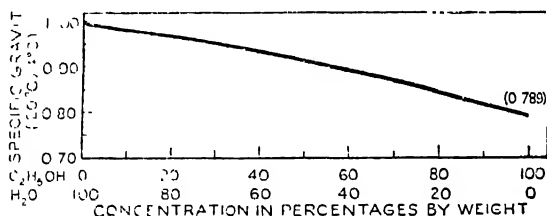


Alcohol is also made to some extent from wood-waste and saw-dust by hydrolytic conversion of their cellulose contents into saccharoids and subsequent fermentation. Dangeville's process for the hydrolysis of cellulose consists in treating the material with concentrated hydrochloric acid in two steps, the first part being accomplished by the action of gaseous acid on the moistened material, and the acid, after absorption and dilution with water, being utilized to carry out

the secondary hydrolysis at the boil. Operating in this way, a yield of 67·6 per cent. of glucose has been obtained from pine wood, 62·59 per cent. from wood pulp, 59·54 per cent. from rye straw, and 70·43 per cent. from bleached sulphite cellulose. Larch wood has proved to be one of the most promising sources of ethyl alcohol as tested by the United States Forests Products Laboratory. The production of ethyl alcohol by thermophilic fermentation of cellulose is discussed by M. K. Veldhuis (*Ind. Eng. Chem.*, **28**, 430 (1936)), and the chemistry of alcoholic fermentation by L. Michaelis (*Ind. Eng. Chem.*, **27**, 1037 (1935)). (See Glucose, and Wood.)

The "Amylo" process carried on near Lille depends upon the use of certain moulds, such as the *Aspergillaceæ*, for saccharifying starch (such as that of maize, rice, potatoes, etc.) instead of malt—the *Rhizopus delemar* or *Mucor boudard* being almost exclusively employed—thus avoiding the formation of the unfermentable dextrins

ETHYL ALCOHOL ( $C_2H_5OH$ )—WATER ( $H_2O$ ) MIXTURES  
SPECIFIC GRAVITY—CONCENTRATION RELATIONSHIP



which result to some extent when malt is used. A mash of sp. gr. 1·060 is made by steaming the starch material under pressure in a cooker, and after injection into the fermenting vessel, is cooled to 40° C., when the active culture of the mould is introduced. The yeast (*Amylomyces*) used for fermenting the material thus prepared exercises its optimum effect in a slightly acid admixture at 38° C., and the process, which takes in all four days to complete, yields up to 97·5 per cent. of the alcohol theoretically obtainable.

The Jerusalem artichoke has long been recognized as a possible raw material for production of power alcohol, and Government experiments have shown a yield of about 18·7 gallons per ton of tubers.

Ethyl alcohol is made in U.S.A. from the ethylene contained in petroleum refinery gases by absorption in 95 per cent. sulphuric acid, and hydrolysing the ethyl sulphate thus produced, by dilution of the acid mixture with water or steaming, thus producing alcohol which is recovered by distillation and regenerating the sulphuric acid.

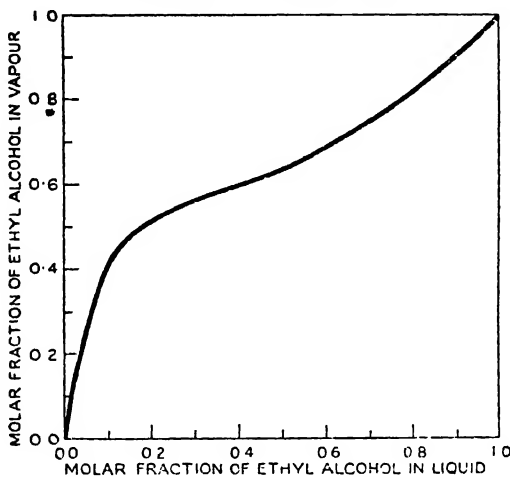
Alcohol can be synthesized from acetylene as produced from calcium carbide, the acetylene thus produced being next transformed into acetaldehyde by hydration in presence of a suitable catalyst such as mercuric oxide in sulphuric acid solution— $C_2H_2 + H_2O = CH_3CHO$ —and by catalytic hydrogenation over reduced copper or nickel or

electrolytic hydrogenation the acetaldehyde is finally converted into alcohol— $\text{CH}_3\text{CHO} + \text{H}_2 = \text{CH}_3\text{CH}_2\text{OH}$ .

In the high-pressure catalytic production of methyl alcohol from hydrogen and carbon monoxide gases some proportion of ethyl alcohol is also formed, and under certain conditions this proportion can be considerably increased.

Although its calorific value is not much more than one-half that of petrol, its efficiency is greater since it can be compressed to a greater extent, and this property of high-ignition temperature under compression is not materially altered by admixture with 20 per cent. benzene

ETHYL ALCOHOL ( $\text{C}_2\text{H}_5\text{OH}$ )—WATER ( $\text{H}_2\text{O}$ ) MIXTURES.  
VAPOUR—LIQUID RELATIONSHIP AT BOILING-POINT  
(PRESSURE: 760 MM. HG)



0.75 Molar fraction is 88.5%  $\text{C}_2\text{H}_5\text{OH}$ —11.5%  $\text{H}_2\text{O}$

0.50 Molar fraction is 72%  $\text{C}_2\text{H}_5\text{OH}$ —28%  $\text{H}_2\text{O}$

0.25 Molar fraction is 46%  $\text{C}_2\text{H}_5\text{OH}$ —54%  $\text{H}_2\text{O}$

or petrol. Such a mixture readily starts in the cold and runs smoothly ; so that if alcohol could be manufactured sufficiently cheaply it would become a serious competitor with petrol as a fuel for internal combustion engines.

Alcohol is soluble in water, and is largely used as a solvent, in the manufacture of explosives, chemicals, perfumes, lacquers, pharmaceutical extracts and tinctures, also as a fuel, in the compounding of drinks, and for preserving anatomical specimens. It would be much more extensively used, but for the legal restrictions on its use which have largely led to the employment of other organic solvents. When alcohol is diluted with water there is a contraction in volume. (See E. F. Armstrong on "Alcohol through the Ages" (*Chem. and Ind.*, 52, K.C.E.—2

251, 279 (1933)) ; *Alcoholic Fermentation*, by A. Harden (Longmans, Green and Co., London) ; *Effects of Alcohol on Man*, by K. and P. H. Kitchin (Victor Gollancz, Ltd., London) ; Fermentations, Fuel (Liquid), Proof Spirit, and Wine.)

**Propyl Alcohol (Normal)** ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ) is a spirituous, colourless liquid which can be obtained from fusel oil. By oxidation it yields propylaldehyde ( $\text{C}_3\text{H}_6\text{O}$ ), and finally propionic acid ( $\text{C}_3\text{H}_6\text{O}_2$ ). (See Isopropyl Alcohol.)

**Butyl Alcohol (Normal)** ( $\text{CH}_3(\text{CH}_2)_3\text{OH}$ ) is a limpid, colourless liquid of b.p.  $118^\circ\text{C}$ ., sp. gr. 0.810, flash-point about  $85^\circ\text{F}$ . ; soluble in water and alcohol, and by oxidation yields butyric acid ( $\text{C}_4\text{H}_8\text{O}_2$ ). It is used as a solvent in the saponification of fats resistant to ordinary alcoholic soda, also to some extent in making fruit essences. Its production from maize is referred to under the heading of Acetone.

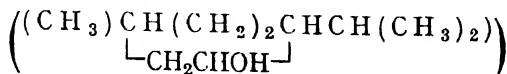
The normal secondary butyl alcohol ( $\text{CH}_3\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$ ) is a thin colourless liquid of pleasant odour, sp. gr. 0.808 and b.p.  $99.5^\circ\text{C}$ ., soluble in water and alcohol, used in perfumery and making fruit essences. The normal iso-butyl alcohol ( $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$ ) is a colourless mobile liquid of sp. gr. 0.805 and b.p.  $107^\circ\text{C}$ ., soluble in water and alcohol, used for the same purposes as the normal secondary alcohol. The tertiary butyl alcohol ( $(\text{CH}_3)_3\text{COH}$ ) is a white crystalline substance of camphor-like odour of sp. gr. 0.786, m.p.  $25^\circ\text{C}$ ., and b.p.  $83^\circ\text{C}$ ., soluble in water and alcohol, used in making fruit essences, etc.

**Amyl Alcohol (Normal)** ( $\text{CH}_3(\text{CH}_2)_4\text{OH}$ ) — The normal amyl alcohol is colourless, of disagreeable odour, b.p.  $138^\circ\text{C}$ ., sp. gr. of 0.817, and flash-point about  $105^\circ\text{F}$ . The ordinary amyl alcohol of commerce is largely  $(\text{CH}_3(\text{C}_2\text{H}_5)\text{CHCH}_2\text{OH})$  as produced in processes of fermentation and contained in fusel oil, particularly that found in the last runnings of fermentation alcohol from potatoes and molasses. It is generally levorotatory in character ; is soluble in water, alcohol, and ether, and of b.p.  $128^\circ\text{C}$ ., and sp. gr. 0.816. There are no less than eight isomeric forms of amyl alcohol of boiling-point varying from  $102^\circ$  to  $138^\circ\text{C}$ ., and several of these are contained in fusel oil, of which, however, the chief constituent is the active amyl alcohol. It is made in large quantities as a solvent of cellulose in making so-called "dope" for use in connection with the manufacture of aeroplanes. (See Dope, Fusel Oil, and "Pentanol.")

**2-Ethyl Hexanol** ( $\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{OH}$ ) boils at  $184.6^\circ\text{C}$ ., and used as a lacquer solvent. Its acetate boils at  $199.3^\circ\text{C}$ ., and is also used as a lacquer solvent.

In **Benzyl Alcohol** ( $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ ) the alkyl residue is replaced by an aromatic nucleus, and this is true of all the alcoholic derivatives of the carbocyclic series, but the alcoholic hydroxyl group is never united directly to a carbon atom of the aromatic ring.

In so-called secondary alcohols like **menthol**



the secondary group  $\text{CHOH}$  may be attached to a non-aromatic cyclic carbon ; they are not oxidizable to acids but to ketones (see Isopropyl Alcohol), while the tertiary alcohols, *e.g.* **trimethyl carbinol** ( $(\text{CH}_3)_3\text{COH}$ ), yield upon oxidation ketones or acids containing fewer atoms of carbon than the parent alcohol.

The glycols or dihydric alcohols can be regarded as derived from paraffins, in which two hydrogen atoms on two different carbon atoms are replaced by two hydroxyl groups, and include **ethylene glycol**, **propylene glycol**, and **butylene glycol**. They are mostly viscid liquids of somewhat sweet taste, readily soluble in water and alcohol. (See Ethylene Glycol.)

Of the trihydric alcohols, **glycerol** (glycerine) is a member and illustrative. (See Glycerol.) (See also Erythritol, and Sorbitol.)

**ALDEHYDES** — A series of organic bodies of the type  $\text{R.C} \begin{smallmatrix} \diagup \text{H} \\ \diagdown \text{O} \end{smallmatrix}$ , where

R is an alkyl or aryl radical, and the group  $\text{—C} \begin{smallmatrix} \diagup \text{H} \\ \diagdown \text{O} \end{smallmatrix}$  is characteristic

of aldehydes. The simplest aldehyde is formaldehyde ( $\text{H.CHO}$ ), followed by acetaldehyde ( $\text{CH}_3\text{CHO}$ ). The simplest aromatic or benzenoid aldehyde is benzaldehyde ( $\text{C}_6\text{H}_5\text{CHO}$ ). See each of these.

The regulated oxidation of a primary alcohol, containing the group  $\text{—CH}_2\text{OH}$ , results in the formation of the corresponding aldehyde. More vigorous oxidation produces the corresponding carboxylic acid. For example :



These aldehydes are easily reconverted into their corresponding alcohols by the action of nascent hydrogen ; thus acetaldehyde is changed back to ethyl alcohol, as shown in the equation :  $\text{CH}_3\text{CHO} + \text{H}_2 = \text{CH}_3\text{CH}_2\text{OH}$ . This can be realized, for example, by passing its vapour with hydrogen gas over finely divided copper or nickel at  $120^\circ$  to  $300^\circ$  C. With copper the yield is 87.6 per cent. at  $200^\circ$  C.

The lower members of the aldehydes, except the gas formaldehyde, are neutral volatile liquids of characteristic odour, soluble in water, with lower boiling points than those of the corresponding alcohols, and are rather easily polymerized. Physiologically, the aldehydes are usually hypnotics, *e.g.*, paraldehyde, and chloral.

**ALDOL** ( $\text{CH}_3\text{CHOH.CH}_2\text{CHO}$ ) — A product which results when acetaldehyde is left in contact with dilute hydrochloric acid or sodium hydroxide. Aldol condensation is a reaction between aldehydes or ketones, occurring without the elimination of any secondary product, thus :  $\text{CH}_3\text{CHO} + \text{HCH}_2\text{CHO} = \text{CH}_3\text{CHOH.CH}_2\text{CHO}$ , where 2 mols. of acetaldehyde condense to form 1 mol. of aldol. (See Aldehydes, and Condensation.)

**ALDOSES** — See Carbohydrates.

**ALDRIN** (1,2,3,4,10,10 — Hexachloro — 1,4,4a,5,8,8a — hexahydro — 1,4,5,8, — dimethanonaphthalene) — An insecticide that is highly toxic to many species.

**ALEMBIC** — An early form of still shaped somewhat like a retort, but in two parts: a gourd-shaped vessel called the *cucurbit*, and a cap carrying a side tube which was the *alembic* proper.

**ALEMBROTH (SALT OF)** — A crystalline compound of mercuric chloride and ammonium chloride ( $2\text{NH}_4\text{Cl}, \text{HgCl}_2, \text{H}_2\text{O}$ ), prepared by mixing solutions of the two salts in suitable proportions.

**ALFA (Alva)** — See Esparto Grass.

**ALFALFA** (*Stipa tenacissima*) — Spanish name for lucerne, used for the same applications as esparto grass. (See Esparto Grass, and Lucerne.)

**ALGÆ** — An order of flowerless plants, including the seaweeds (*fucus*) and the fresh-water confervæ. (See Seaweeds, and Vegetation.)

**ALGIN (Norgin)** — A gelatinous (albuminous) material, being a sodium salt of alginic acid (obtained from seaweeds), used as an adhesive and food. It is made by soaking the marine algæ for twenty-four hours in a 1 per cent. solution of sodium carbonate, filtering the viscous liquor through cloth, and precipitating it therefrom by dilute sulphuric acid, washing and drying. The compounds of algin give very viscous solutions, and are valuable as sizings for textiles and paper, as thickenings for printing colours, and as proofings for interior walls and ceilings. The sodium compound is soluble in water, and a 5 per cent. solution is so viscous that it can hardly be poured out from its containing vessel. The heavy metallic compounds are insoluble in water, but some are soluble in ammonia, and these solutions are used as waterproofing materials for textiles.

**ALICYCLIC** — The distinctive term applied to cycloparaffin hydrocarbons and their derivatives. The word is a contraction of *aliphatic-cyclic*. (See Cyclic.)

**ALIPHATIC** — The distinctive term applied to molecules whose carbon atoms are arranged only in chains, as distinguished from those whose carbon atoms are in rings, *i.e.*, cyclic. The fatty acids are, for example, members of the aliphatic series. (See Chains.)

**ALiquot** — A definite proportion of a given quantity.

**ALIZARIN** (1, 2-Dihydroxyanthraquinone) ( $\text{C}_6\text{H}_4(\text{CO})_2\text{C}_6\text{H}_2(\text{OH})_2(1, 2)$ ) — An important colouring matter, prepared from the roots of the madder plant (*Rubia tinctorum*), in which it is contained in the form of a glycoside, and now made on an extensive scale by a synthetic process from anthracene. Anthracene is oxidized into anthraquinone; the product is sulphonated and then fused with caustic soda and potassium chlorate, after which the fused mass is dissolved in hot water and the alizarin precipitated out of solution by addition of hydrochloric acid. It is prepared from phthalic anhydride and *o*-dichlorobenzene. It crystallizes in fine red prisms and needles, of m.p.  $289^\circ\text{C}$ .; is sublimable, and soluble in alcohol and ether, but only to a small extent in

water. It was the first naturally occurring dye to be synthesized. With metallic oxides it gives "lakes" of varying hues, which are used in dyeing. (See Madder.)

**ALKALI WASTE** — The residual matter or by-product from the manufacture of sodium carbonate by the old Leblanc process. For every ton of soda ash produced there are from one and a half to two tons of waste. Many processes have been devised for the extraction or recovery of the sulphur it contains in combination with calcium—viz., 15 to 20 per cent.—and of these the most important is the "Chance" process, which, however, is applicable only to recently made waste as distinct from the old accumulated masses lying in manufacturing areas, and which rapidly suffer chemical changes by atmospheric action. (See Sodium Carbonate, and Sulphur.)

**ALKALIMETRY** — The determination of amount of alkali contained in a solution by titration with a standard acid solution. (See Analytical Chemistry.)

**ALKALIS** — Hydroxides of the alkaline metals. (See Acids and Bases.)

**ALKALOIDS** — Organic compounds containing nitrogen and having basic (alkaline) properties. The name is generally restricted to compounds occurring naturally in plants. Although a few are relatively simple compounds containing only carbon, hydrogen, and nitrogen (e.g., nicotine) most alkaloids are complex compounds, and frequently contain oxygen in addition. Most alkaloids are tertiary amines, and may be considered as derivatives of ammonia ( $\text{NH}_3$ ) in which the hydrogens are replaced by organic radicals. Chemically, many alkaloids resemble ammonia in their strongly alkaline reaction, and in forming compounds with acids. All alkaloids are optically active, and as a class are bitter to the taste and frequently highly poisonous.

The alkaloids are important in medicine because of their physiological properties, and many drugs depend for their action on the presence of these compounds. In their natural state in plants they are frequently combined with organic acids, such as citric, malic, and tannic acids. To separate the alkaloids in a pure state, the plant material is macerated with lime or other alkali, and the free alkaloid extracted with alcohol, benzene, or other solvent. Upon acidification with an acid such as hydrochloric, the hydrochloride of the alkaloid may be separated by extraction with water. Occasionally the alkaloids can be extracted directly from plant tissues with dilute acids. Nicotine and other volatile alkaloids may be separated by steam distillation following the treatment of the plant tissue with alkali.

The most important alkaloids are aconitine, atropine, brucine, codeine, coniine, morphine, nicotine, papaverine, pilocarpine, quinine, solanine, and strychnine (which see). (See "The Micro-Detection of Alkaloids," by G. Lander (*Analyst*, **55**, 474 (1930)); "Systematic Scheme of Identification of Alkaloids," by K. E. Jackson (*Ind. Eng. Chem., Anal. Edit.*, **10**, 380 (1938)); *The Plant Alkaloids*, by T. A. Henry (J. and A. Churchill, London); Allen's *Commercial Organic*

*Analysis*, volume on "Vegetable Alkaloids" (J. and A. Churchill, London); "Physical Constants of Alkaloids" in *Handbook of Chemistry*, by N. A. Lange (Handbook Publishers, Inc., Sandusky, Ohio); *The Alkaloids: Chemistry and Physiology*, by R. H. F. Manske and H. L. Holmes (Academic Press, New York); *The Manufacture and Chemistry of the Alkaloids*, by F. Hamerslag (D. Van Nostrand Co., New York); also Amines, and Ptomaines.)

**ALKANET (Alkanna)** — An ancient dyestuff in the form of a dark red amorphous powder, prepared from the roots of *Alkanna tinctoria*. It exhibits a green iridescence; is used by natives in the East for dyeing the nails, teeth, hair, and garments; also colouring oils red.

**ALKOXIDES** -- See Alcoholates.

**ALKYL (Radicals)** — The monovalent groupings ( $C_nH_{2n+1}$ ), such as methyl and ethyl, which form the radicals of the monovalent alcohols. The group is frequently represented by the radical R. The process of introducing an alkyl radical is called alkylation, and a common source is (1) the proper alcohol, involving the elimination of H atom usually by OH radical (whereby water is formed) of the substance to be alkylated, (2) the proper haloid, involving the elimination of Cl or Br atom usually by Na atom (whereby sodium chloride is formed) or (3) the proper sulphate, involving the elimination of  $SO_4$  radical (whereby  $NaRSO_4$  is formed). Lead tetraethyl ( $Pb(C_2H_5)_4$ ) is a metallic alkyl.

**ALKYLATION** — See Petroleum (Cracking).

**ALLANITE** — A natural complex silicate. (See Orthite.)

**ALLETHRIN** — The allyl homologue of Cinerin I (see Pyrethrum); used as an insecticide.

**ALLOBARBITONE ("Dial")** ( $C_{10}H_{12}O_3N_2$ ) — A white crystalline substance, namely, 5,5-diallylbarbituric acid; slightly soluble in water, soluble in alcohol and ether; m.p.  $172^\circ$  to  $174^\circ$  C. Used in medicine as a sedative and hypnotic.

**ALLOPHANE** — A mineral hydrated aluminium silicate of sp. gr. 1.75.

**ALLOTROPY** -- Allotropy is a special case of a general phenomenon known as *polymorphism*. Polymorphic forms are solid states of the same ultimate chemical composition differing among themselves in crystalline form, free energy and other chemical and physical properties, but yielding identical gaseous and liquid phases upon evaporation or fusion.

When polymorphic forms are composed of a single element such as carbon, sulphur, phosphorus, or tin the forms are said to be *allotropic*. If the forms are composed of compounds such as ice, ammonium nitrate, or mercuric iodide they are said to be *polymorphic*. Every polymorphic form exists as a separate phase. The number of polymorphic forms that exist for a given component is the number of solid phases that exist. In cases where there is a definite transition temperature between forms— as, for example, grey and white tin—the

form is said to be *enantiotropic*. When one form is more stable at all temperatures than the other it is said to be *monotropic*, as in the case of explosive antimony. (See A. Smits, *Theory of Allotropy* (Longmans, Green and Co., London).)

**ALLOXAN** ( $C_4H_2N_2O_4$ ) — A derivative of uric acid, which yields urea by the action of barium hydroxide.

**ALLOYS** — Combinations of two or more elements having metallic properties. They are further characterized by the formation of either wide or restricted solid solutions, and/or intermetallic, electron, or normal valency type of compounds. Alloying affects the chemical, mechanical, and physical properties of the solvent metal, the extent of which is dependent on the constitutional nature of the solid solution and/or on the existing type of compound formation. (A fundamental consideration of factors influencing the alloying nature of metals is found in the references listed under Physics of Metals, and Crystal Chemistry.)

The most important industrial alloys are those in which aluminium, copper, iron, lead, magnesium, nickel, tin, and zinc are the principal components. In other alloys for special applications, bismuth, gold, silver, and platinum are some of the solvent metals. Some specific examples of these alloys are cited later.

The use of the microscope and the study of the thermal or pyrometric behaviour of alloys on heating and cooling afford the most important information respecting alloys, the thermal examination sufficing in many cases to determine the composition. The eutectic temperatures of alloys correspond with the cryohydric temperatures of ordinary solutions. (See Solution.)

Eutectic alloys are brittle, and have melting-points lower than either of their constituent metals. (See Eutectic.)

Wood's fusible metal, for example, an alloy of lead, bismuth, tin, and cadmium, melts at  $60.5^\circ C.$ , while none of the individual components melts below  $232^\circ C.$  The electrical conductivity is, as a rule, lower than the mean as calculated from the component parts, since such alloys acting as thermo-couples exercise force in opposition to that producing the current.

Alloys of the solid solution class—that is, those in which the dissolved substances cannot be detected or mechanically separated—such as brass and German silver, exhibit properties like those of single metals, can be cold-rolled and drawn, and are harder than the constituent metals.

Antifriction alloys, extensively used for bearings, are composed of tin and antimony with either copper or lead, as they combine hardness with plasticity.

The crystal structures found in pure metals become modified in alloys, particularly so in the solid-solution variety, where the atoms of the alloying element enter into the structure and produce certain minute changes, influencing their behaviour on melting, freezing, and in other phenomena.

In making alloys, the metal of highest melting-point is first fused and the others added in order of their melting points.

So-called *German silver* is a mixture of copper, zinc, and nickel; and *brass* consists of about 2 parts copper and 1 part zinc. The British gold coin consists of pure gold 22 parts and 2 parts alloy of silver and copper.

Descriptions of various alloys will be found under the headings of the metals used in compounding them, and some of the better-known ones are shown in tabulated form below.

Alloy	Cadmium	Copper	Zinc	Tin	Antimony	Nickel	Lead	Bismuth	Iron
Aluminium bronze ..	—	9	1	—	—	—	—	—	—
Muntz metal ..	—	3	1	—	—	—	—	—	—
Yellow brass ..	—	66	33	—	—	—	—	—	—
Tin or red brass ..	—	82	15	3	—	—	—	—	—
Mosaic gold ..	—	50	50	—	—	—	—	—	—
Britannia metal—									
(a) English ..	—	1	—	94	5	—	—	—	—
(b) sheet ..	—	1.6	—	90.6	7.8	—	—	2	—
(c) cast ..	—	0.2	—	90.6	9.2	—	—	—	—
Bell metal ..	—	80	20	—	—	—	—	—	—
Bronze (for statues)	—	91.4	5.53	1.7	—	—	1.37	—	—
" (for cannon)	—	90.0	—	10.0	—	—	—	—	—
German silver ..	—	50	25	—	—	25	—	—	—
Gun metal ..	—	9	—	1	—	—	—	—	—
Type metal ..	—	—	—	5	20	—	75	—	—
Stereotype metal ..	—	—	—	3	18	—	112	—	—
Pewter (a) ..	—	—	—	4	—	—	1	—	—
" (b) ..	—	1.8	—	89.4	7.0	—	1.8	—	—
Wood's fusible metal	1	—	—	1	—	—	2	4	—
Minofo metal ..	—	3.3	10	68.5	18.2	—	—	—	—
Monel metal ..	—	33	—	—	—	60	—	—	6.5

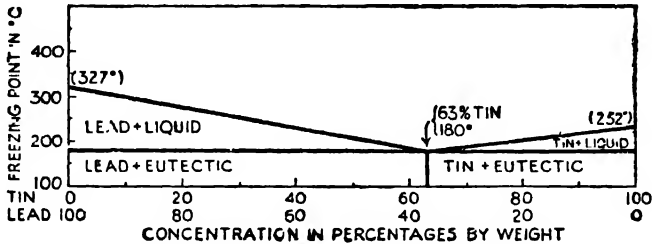
An alloy of 85 per cent. lead and 15 per cent. magnesium when exposed to moist air undergoes rapid oxidation, swelling up and falling to a black powder in course of a few hours. This alloy decomposes water, liberating hydrogen, and particularly so when the proportion of magnesium is increased to 30 per cent.

There are alloys of nickel and chromium of high tensile and acid-resisting strength which will withstand temperatures of over 1,260° C. without oxidation and consequent scaling. Most of the commercially useful ones fall within about 10 per cent. and 50 per cent. chromium respectively. Furnace parts of such character usually contain from 25 to 35 per cent., while resistance wire is made from the binary alloy containing from 10 to 15 per cent.

Nickel-chromium-iron alloys are also extensively employed, having great heat and acid-resisting properties, the percentage of iron depending upon the magnitude of the stress they have to bear as used. The "Emperor" alloy will, it is claimed, resist a temperature of 1,750° to 1,800° F., the tensile strength remaining at 30,000 pounds per square inch, being, when cold, approximately twice that of cast iron.

### TIN-LEAD MIXTURES

#### FREEZING-POINT—CONCENTRATION RELATIONSHIP



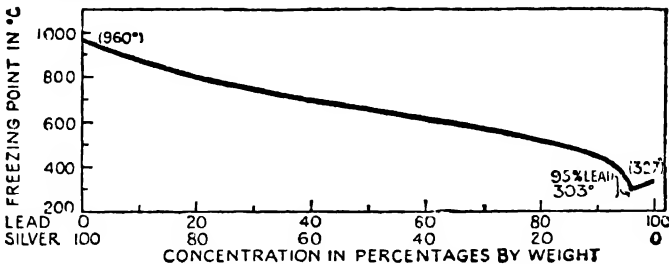
Common Solder : 50 per cent. tin *plus* 50 per cent. lead.

Solders in general : 67 to 33 per cent. tin *plus* 33 to 67 per cent. lead respectively.

Other elements are also present in many of these alloys, including carbon, silicon, aluminium, manganese and copper, according to the application to be made of them. They are not sufficiently resistant to be suitable for the construction of chemical plant required to deal with acid liquors at above or in the neighbourhood of 100° C. The

### LEAD-SILVER MIXTURES

#### FREEZING-POINT—CONCENTRATION RELATIONSHIP



composition, and thermal and mechanical qualities of 258 alloys and metals are discussed in *Chem. Mct. Eng.*, 39, 497 (1932).

Aluminium is extensively used in making a number of alloys with copper. (See Bronzes.) *Magnalium* is an alloy of aluminium with from 10 to 30 per cent. of magnesium; silver-white, strong, ductile, easily cast, and of sp. gr. from 2.5 to 2. When 10 per cent. magnesium is present,

the alloy has a melting-point of about  $600^{\circ}\text{C}.$ ; is lighter than aluminium and of good workability. Aluminium alloy A, which has been found to meet requirements of the motor and other industries, consists of aluminium, 87.30 per cent.; copper, 4.68 per cent.; zinc, 2.37 per cent.; nickel, 1.85 per cent.; lead, 1.51 per cent.; magnesium, 1.34 per cent.; iron, 0.51 per cent.; silicon, 0.39 per cent.; tin, 0.050 per cent.; and a trace of manganese.

Alloys of aluminium and magnesium of the compositions  $\text{Al}_3\text{Mg}_2$  and  $\text{Al}_2\text{Mg}_3$  have been described, and other magnesium alloys adapted to special applications are made containing small percentages of copper, manganese, nickel, lead, tin, and iron. There are definite alloys of copper with zinc and tin respectively, having the formulæ  $\text{CuZn}_3$  and  $\text{Cu}_3\text{Sn}$ , and others recognized as true chemical compounds include  $\text{Al}_3\text{Mn}$ ,  $\text{Cd}_3\text{Tl}$ ,  $\text{Hg}_6\text{Na}$ ,  $\text{Hg}_2\text{Na}$ ,  $\text{PtHg}_2$ ,  $\text{PtZn}$ ,  $\text{PtSn}$ ,  $\text{SnCu}_3$ ,  $\text{Zn}_3\text{Hg}$ , and  $\text{AuCu}$ .

A tertiary alloy of lead, with 2 per cent. barium and 1 per cent. calcium (Frary Metal), was found during World War I to have value as a bearing metal and, in view of the shortage of antimony, in making shrapnel bullets. Alloy steels are dealt with under heading of Iron.

Among other alloys are "Alargan" (aluminium and silver), "Platalargan" (aluminium, silver, and platinum), and "Platnik" (platinum and nickel). "New Metals and Alloys from Lead, Tin, Zinc, and Antimony" is the subject of a paper by G. O. Hiers in *Ind. Eng. Chem.*, **28**, 1406 (1936), and "Beryllium-Copper Alloys" of one by H. F. Silliman in *Ind. Eng. Chem.*, **28**, 1424 (1936).

**Soldering** means fusing together the surfaces of the same or different metals by means of an interposed alloy which must be more fusible than the two metals to be joined, and have an affinity for both of them. Solders may be described as fusible alloys, classed respectively as "hard" or "soft" according to their melting points, the former comprising various brazing, silver, and gold solders, and the latter being, in the main, lead-tin alloys melting below  $300^{\circ}\text{C}.$  Hard solder, used in brazing brass, consists of equal parts of copper and zinc, while for copper and iron a mixture of 1 part copper and  $\frac{3}{4}$  part zinc is used.

For soldering or brazing steel a solder of 19 parts silver with 1 part each of brass and copper is used. Cadmium is used to a considerable extent in compounding lead-cadmium-zinc alloys for use in general soldering work: one recommended formula being Pb, 90.8 per cent.; Cd, 7.8 per cent.; and Zn, 1.4 per cent. A solder composed of 4 per cent. Hg, 3 per cent. Sn, and 93 per cent. Pb has found favour in the United States in respect of ships' fittings, such as galvanized-iron tubes and sheets, the joints holding well when the soldered parts are bent. The best solder for aluminium is stated to consist of a mixture of about 55 per cent. germanium and 45 per cent. aluminium. (See "Alsoco.")

There are many factors to be considered in connection with the use of solders, such as composition, fusibility, range of temperature, solidification, hardness, etc., and various specifications are given by the B.S.I. (B.E.S.A.).

Rostovsky and Lüder opine that the joining power of a solder may be

due to : (1) The solder and the object forming solid solutions together, such as brass solder and copper ; (2) the formation of inter-metallic compounds of the solder and the object, such as tin-lead solder and copper ; and (3) the solution of the object metal in the solder, while, upon cooling, the dissolved metal crystallizes out on the solder layer—e.g., tin-solder and zinc.

Fluxes are used for cleaning metal surfaces. (See Fluxes.)

(See *Engineering Metals and Their Alloys*, by Carl H. Samans (Macmillan, New York) ; *Structure and Properties of Alloys*, by R. M. Brick and A. Phillips (McGraw-Hill Book Co., New York) ; *The Theory of the Properties of Metals and Alloys*, by N. F. Mott and H. Jones (Oxford Univ. Press) ; "Alcobronze" (under Copper), "Alnico," "Aterite," Babbitt Metal, "Carbobronze," "Coronium," "Duralumin," "Durimet," Dutch Metal, "Elinvar," Ferro-Alloys, "Frery Metal," Fusible Metal, "Invar," Iron, "Ironac," "Magnalia," "Monel," Mosaic Gold, "Ohmal," "Pallas," "Permalloy," Phosphor Bronze, "Pinchbeck," "Platinite," "Platinoid," "Platinor" (under Platinum), Rustless Steel, Silicon Bronze, "Silumin," "Silveroid," "Speculum," "Staybrite," "Stellite," and Welding.)

**ALLSPICE OIL** — See Pimento Oil.

**ALLYL ALCOHOL** ( $\text{CH}_2 : \text{CH}.\text{CH}_2\text{OH}$ ) — A limpid, lachrimatory liquid, b.p.  $97^\circ \text{C}$ ., sp. gr. 0.854. It is miscible with alcohol and ether, and is oxidized to glycerol by alkaline permanganate. It has been used in medicine, and occurs naturally as the isothiocyanate ester in volatile oil of mustard.

**ALMOND OIL** -- A fixed oil obtained by expression from the dried ripe seeds of *Prunus communis* var. *amara* (Bitter Almond) and var. *dulcis* (Sweet Almond), both of which contain about 50 per cent. of the oil. It has a yellowish colour and a slight, characteristic odour ; sp. gr. 0.915 to 0.920. It consists mainly of olein and is used in cosmetics and medicine. An analysis of this oil gave the composition as 83.73 per cent. olein, 14.77 per cent. linolein, and 1.5 per cent. glycerides of saturated acids. (See "Notes on Histology of the Almond," V. A. Pease, *Analyst*, 56, 187 (1931).)

**Bitter Almond Oil** is a volatile oil obtained by maceration and distillation from bitter almond cake. It occurs as an almost colourless liquid, having a characteristic odour and ref. ind. 1.534 to 1.542 at  $20^\circ \text{C}$ . ; sp. gr. 1.045 to 1.060 at  $15^\circ \text{C}$ . It is soluble in alcohol and ether, sparingly soluble in water and is used as a flavouring agent. Its fragrant odour is due to benzaldehyde which it contains to the extent of about 90 per cent., and is formed, together with hydrogen cyanide, benzaldehyde-cyanhydrin and a sugar, gentiobiose (structurally identical with maltose), by the action of emulsin on amygdalin during the maceration process. The synthesis of amygdalin from gentiobiose has been effected by Haworth. (See Benzaldehyde, Glycosides, and Nitrobenzene.)

**"ALNICO"** — Permanent magnetic alloy containing approximately 20 per cent. nickel, 12 per cent. aluminium, 5 per cent. cobalt, 0.4 per

cent. manganese and silicon combined, 0.15 per cent. carbon (max.), and the balance iron. The magnets are made either by sand casting, precision casting, or sintering. They are hard, comparatively brittle, and non-machinable. They have a high degree of magnetizability after heat treatment and suffer little or no magnetic loss upon mechanical impact.

**ALOES (Bitter Aloes)** — The inspissated juice of various species of *Aloe*, containing aloin. Used in medicine. Socotrine and Zanzibar aloes are both prepared from *Aloe Perryi* in East Africa. Curaçao aloes is obtained from *Aloe vera* var. *officinalis* on the island of Barbados and is sometimes called Barbados aloes. In addition to barbaloin, it contains isobarbaloin which is not present in other varieties of aloes. Cape aloes, from *Aloe ferox*, is prepared in Cape Colony. In addition to its use in medicine, aloes is used in dyeing, for which purpose many other inferior varieties are employed. (See *Chem. Trade J.*, **90**, 12 (1932); Fairbairn on "The Microscopy of Common Commercial Varieties of Aloes" (*Pharm. J.*, **102**, 381 (1946); Gardner and Campbell on the hydrolysis of aloins from various sources in *J. Amer. Chem. Soc.*, **64**, 1378 (1942).)

**ALOIN** ( $C_{21}H_{20}O_9$ ) — A mixture of the crystalline active principles of *Aloe*, obtained by extraction with boiling acidified water and subsequent crystallization. It is obtained chiefly from Curaçao aloes, but other varieties may also be used. Samples obtained from Curaçao aloes consist of approximately equal proportions of barbaloin,  $C_{21}H_{20}O_9$ , and isobarbaloin. It is soluble about 1 in 130 of water and in alcohol, formamide, and alkalis; insoluble in ether, chloroform, and benzene. Used in medicine as a purgative. (See Gibson and Simonsen, *J. Chem. Soc.*, **1930**, 553; E. Léger, *Brit. Chem. Abstracts*, **A**, **1931**, 490; and Smith, Jordan, and De Kay on "The Extraction of Aloin from Aloes" in *J. Amer. Pharm. Assoc.*, **33**, 57 (1944).)

**"ALOXITE"** — See Abrasives.

**ALPHA PARTICLE** — Identified by Rutherford in 1903 as a helium nucleus. Mass 4, charge two units positive. In 1919 Rutherford used alpha particles from radium C to produce the first artificial nuclear reaction, namely, the conversion of nitrogen into oxygen. (See Nuclear Chemistry, and Radioactivity.)

**"ALSO CO"** — An aluminium solder requiring no flux. It comes in three analyses with melting points from 220° to 385° C., with the lowest melting point type used for joining thin wires or delicate parts. The others are intended for use in repairing aluminium castings, sheet, and extruded shapes. The selection of solder depends on the mass of the part. (See "An Aluminium Solder That Requires No Flux" (*Materials and Methods*, **25**, 81 (May, 1947).)

**ALUDEL** — A pear-shaped earthenware pot with an open neck at each end so that a series may be connected together. Formerly used in Spain for condensing the vapours of mercury distilled from its ores.

**ALUM (AMMONIA)** — Ammonium aluminium sulphate.

**ALUM (CHROME)**, or **Potassium Chromium Alum** ( $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$ ), is prepared by the addition of sulphuric acid to potassium dichromate ( $K_2Cr_2O_7$ ) dissolved in water, and then reducing it by the passage of sulphur dioxide gas, with the result that the two sulphates of potassium and chromium are left in solution, from which the alum can be crystallized out in the form of dark plum-coloured octahedral crystals. It is used in paper making, sugar refining, ink making, as a chrome-tanning material, and in the textile industry as a mordant.

**ALUM (IRON)** — Ammonium ferric sulphate. (See Iron.)

**ALUM SHALE** — See Aluminium.

**ALUMINA** — Aluminium oxide.

**ALUMINIUM (Al) and its Compounds** — Atomic weight 26.97. See Elements for other data; also Alumina, Calcium (p. 139); and accompanying Charts. Aluminium is a trivalent metal found very abundantly in nature in a state of combination, but not in the metallic state. It occurs as a phosphate in *wavellite*, and combined with oxygen as alumina ( $Al_2O_3$ ), it forms the substance of *emery* and, in purer forms, the precious stones known as the *sapphire* and *ruby*, both of which are now produced commercially by the fusion of pure alumina in a specially constructed electric furnace, and are as good in all respects as the natural gems, with which they are identical in composition and properties.

In combination with silica, aluminium exists as *allophane*, clays, and *leucite*, and in the forms of *gibbsite* ( $Al_2O_3 \cdot 3H_2O$ ), *diaspore* ( $Al_2O_3 \cdot H_2O$ ) and as a hydrated oxide *bauxite* ( $Al_2O_3 \cdot 2H_2O$ ), from which last-named mineral the metal is chiefly manufactured by an electrolytic process. (See also Fluellite.)

Bauxite occurs in large deposits in many of the American States, France, Iceland, Calabria, Styria, the Gold Coast Colony, India, British Guiana, Montenegro, etc., and the Narracan deposit found in Victoria (Australia) has an alumina content of 52 to 59 per cent.

*Leucite* can be utilized by a variety of processes as a source of alumina, potash, and silica. (See Leucite.)

There are several varieties of bauxite—viz., a white quality containing some 60 per cent. alumina, a little iron, and no silica, which is used for making aluminium salts and alum; a red variety of about the same alumina content, but containing a little silica, used for manufacturing metallic aluminium; and another white kind containing only 45 per cent. alumina and much silica, which is used more for making refractories. Sodium sulphide has so far proved to be the most effective agent for conditioning the pulp in experiments on the treatment of bauxite high in silica content. As a colloidal absorbent acting as a decolourizer and desulphurizing agent bauxite is used for purifying mineral oil. (See *The Industrial Uses of Bauxite*, by N. V. S. Knibbs (Ernest Benn, Ltd., London).)

To prepare metallic aluminium, alumina made from bauxite and dissolved in fused *cryolite*—a double fluoride of aluminium and sodium ( $Na_3AlF_6$ ) occurring only in Greenland—is subjected to electrolysis

in iron pots lined with carbon, carbon rods being used to carry the current; the power used for generating the electric current (by dynamos) being that of falling waters as utilized at Niagara, the falls of the Rhine at Schaffhausen, Kinlochleven and Lochaber in Scotland, in Quebec and British Columbia, Canada, and in Oregon and Washington, U.S.A. In this way, the aluminium oxide is decomposed, the melted metal collects at the bottom of the pots and oxygen liberated at the carbon anodes forms carbon monoxide.

The metal can also be obtained from clay or alunite by a process commencing with ignition, then resolution into sulphate by means of sulphuric acid, followed by conversion into ammonia alum by addition

### ALUMINIUM-CONTAINING SUBSTANCES

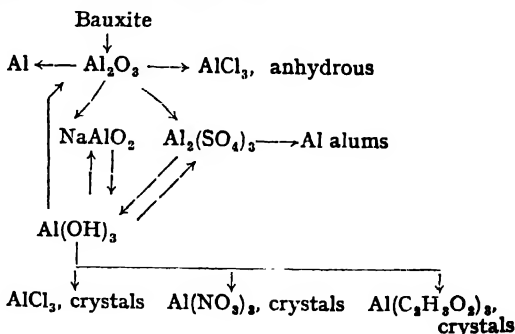
#### *Charts showing Principal Applications*

Arranged by the Editor.

#### CHART I.—OF NATURAL OCCURRENCE

Principal Uses	As Aluminium Oxide (principally)	As Aluminosilicates
Gems	Corundum	Feldspars—principally
Abrasives	Emery	potassium aluminosilicate
Ores of aluminium	Ruby (red)	Micas—principally potassium aluminosilicate
Aluminosilicates	Sapphire (blue)	Leucite — principally potassium aluminosilicate
	Oriental amethyst (purple)	Sillimanite—principally aluminium silicate
	Oriental emerald (green)	Igneous Rocks (principal exception, quartz)
	Oriental topaz (yellow)	Soils
	As Aluminium Phosphate (principally) Turquoise (blue to green)	Clay and Kaolinite—principally aluminosilicic acid
Aluminium element	As Sodium Aluminofluoride (principally) Cryolite	
8% of the earth's crust	As Basic Potassium Aluminium Sulphate (principally) Alunite	
Or, when expressed as $\text{Al}_2\text{O}_3$ , about 15% of the earth's crust	As Hydrated Aluminium Oxide (principally) Bauxite. (See Chart II, following)	

#### CHART II.—OF MANUFACTURE



(See also corresponding Charts of Silicon.)

Aluminium "has come as far in half a century as many other metals advanced in 5,000 years."

## ALUMINIUM AND BAUXITE, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country			Aluminium Metric Tons		Bauxite (Pure $Al_2O_3$ contains 53% Al) Metric Tons
Germany-Austria	..	..	160,000		20,000
France	..	..	43,000		687,000
Norway	..	..	28,000		
Switzerland	..	..	27,000		
Italy	..	..	26,000		381,000
United Kingdom	..	..	22,000		
Sweden	..	..	2,000		
Hungary	..	..	1,000		556,000
Yugoslavia	..	..	1,000		355,000
				310,000	
Greece	..	..	None		172,000
U.S.S.R.	..	..		43,000	250,000
U.S.A.	..	..	137,000		376,000
Canada	..	..	61,000		
				198,000	
Netherlands Guiana	..	..	None		424,000
British Guiana	..	..	None		391,000
Brazil	..	..	None		10,000
Japan	..	..		16,000	
Netherlands Indies	..	..	None		238,000
Malaya	..	..	None		56,000
British India	..	..	None		15,000
Indochina	..	..	None		2,000
Australia	..	..	None		4,000
Sum of above				567,000	3,937,000

WORLD PRODUCTION, approximately the above.

of ammonium sulphate, and by action of dry ammonia gas at  $75^{\circ}\text{C}$ . conversion into aluminium hydroxide and ammonium sulphate. The hydroxide is then ignited, forming alumina, from which the metal is made. Various processes proposed and in use for refining aluminous ores are reviewed by C. L. Mantel in *Industrial Electrochemistry* (McGraw-Hill Book Co., New York).

The metal is extremely light, being about one-third the density of iron, and is of the colour of tin. It is very malleable, ductile, does not tarnish when exposed to dry air, although it is subject to surface oxidation in moist air, particularly in hot climates. It is a good conductor of electricity, and is extensively used in the construction of many articles both for manufacturing and household employment, such as storing spirituous liquors and milk, on account of being resistant to corrosion and not toxic. (See *A Select, Annotated Bibliography on the Hygienic Aspects of Aluminium and Aluminium Utensils* (Bibliogr. Series Bull. 3, Mellon Institute of Industrial Research, Pittsburgh).)

The metal is largely used in making chemical plant, being stable against essential oils and ammonia (of all strengths and at all temperatures), and when quite pure it can be employed in respect of nitric acid but not hydrochloric acid. Aluminium is also used in the construction of buildings and aeroplanes, and alloyed with various other metals it can be usefully employed where lightness combined with strength are desirable qualities. It is prepared in standardized sheets of various thickness for the making of cans suitable for the preservation of foods and other purposes. In the form of powder it finds use as an ingredient of certain explosives (see Ammonal), and in the "thermit process." It is largely employed in the metallurgy of other metals; in making fireworks, paints, and explosives; and mixed with oil as a paint for iron exposed to the air. Vaporized aluminium condensed on glass is used in reflectors for lamps, telescopes, and optical apparatus. As solder for aluminium, various compositions of zinc-tin and zinc-tin-aluminium are stated to give the best results. (See "Alsoco.") It is not proof against hot acetic acid in dilute solutions or barium chloride, and must be ruled out in respect of hot solutions of tartaric acid, ferro- and ferri-cyanides. The solvent action of washing soda on aluminium utensils is prevented by addition of a small amount of sodium silicate to the washing water (as little as 0.05 per cent.). Anodic oxidation produces a surface on aluminium which can be coloured.

In combination with copper, it forms an alloy known as *aluminium bronze*, which makes good castings. This is manufactured by heating a mixture of alumina in the form of *corundum* with charcoal and granulated copper in an electric furnace, in which process the carbon is burned out of the mixture by the oxygen of the alumina ( $\text{Al}_2\text{O}_3$ ), and the copper combines with the metallic aluminium. An alloy of 85 per cent. aluminium, 12.5 per cent. zinc, and 2.5 per cent. copper has proved very successful for general castings, crank cases, pump-bodies, and carburettors. "Aluminium and Its Alloys" is the subject of a paper by W. L. Fink in *Ind. Eng. Chem.*, **28**, 1402 (1936).

(See *The Aluminium Industry*, by J. D. Edwards, F. C. Frary, and Z. Jeffries (McGraw-Hill Book Co., New York); *Aluminum: An Industrial Marketing Appraisal*, by N. H. Engle, H. E. Gregory, and R. Mosse (Richard D. Irwin, Chicago); *Metallography of Aluminum Alloys*, by L. F. Mondolfo (John Wiley and Sons, New York); *The Properties of Aluminium and Its Alloys* (Aluminium Development Association, London); and other references under Physical Metallurgy.)

**Aluminium Oxide** or **Alumina** ( $\text{Al}_2\text{O}_3$ ) and the hydroxide ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) are used as mordants in dyeing and calico printing owing to their property of forming insoluble compounds known as "lakes" with vegetable colours, thus fixing them in the tissues undergoing treatment and making them washable or "fast." The hydroxide can be prepared by adding ammonia to a solution of alum, as a white precipitate, which can be rendered anhydrous by drying and heating.

A dry process for the preparation of alumina involves furnacing bauxite (which must contain less than 3 per cent. of free silica) with soda, and subsequent extraction of the sodium aluminate by leaching with water, and there is a wet process in which the mineral is first heated under pressure with a solution of caustic soda. From these solutions the alumina is obtained by two distinct methods. In the one, carbon dioxide gas is blown into the solution, thus precipitating the hydroxide, and in the other the solution, after dilution, is stirred with a small quantity of hydrated alumina, in which case a large proportion of the alumina in solution is precipitated, leaving a liquid which, after concentration, is used for attacking a fresh quantity of bauxite.

A process is used in Norway for producing alumina from bauxite, by leaching with a 30 per cent. nitric acid solution, which dissolves the aluminium, calcium, and part of the iron contents, leaving the silica and the rest of the iron undissolved. The iron in solution is then removed, the liquid evaporated to dryness, and the residue heated to such an extent that the aluminium salt only is decomposed. The nitrogen oxides driven off in this operation are recovered as nitric acid, and the alumina is employed for the manufacture of the metal and its various compounds.

**Activated Alumina** is an aluminous material consisting of partially dehydrated aluminium hydroxide, having a high porosity and a permanent physical structure. It is used for the removal of water vapour from gases and vapours, for the selective adsorption of certain gases, especially those of high boiling-point, and as a catalyst or a catalyst carrier. See *Ind. Eng. Chem.*, **28**, 947 (1936).

**Corundum**, a nearly pure natural oxide of aluminium of density 3.9 to 4.1 occurs in crystallized form No. 3, hard enough to cut glass; it is now made by an electrical process on a considerable scale, and is largely used for polishing purposes. (See also Emery.)

**Aluminium Chloride** ( $\text{AlCl}_3$ ) is a white, volatile, solid substance produced by heating powdered metallic aluminium, or a mixture of alumina and charcoal, in a current of chlorine. The "McAfee" process for its cheap production from bauxite by means of chlorine is described in the *Ind. Chem.*, **5**, 391 (1929), in an article reproduced

from *Chem. and Met. Eng.* of July, 1929, 422. Bauxite ore is briquetted with good coking coal and the briquettes then heated to about 1,500° F. to get rid of hydrocarbons, after which the resulting carbonized briquettes are chlorinated at about 1,600° F. The product is pure enough for use in the petroleum-cracking industry, for which the bulk of it is used. (See "Action of Aluminium Chloride on Paraffins," by V. N. Ipatieff and A. V. Grosse (*Ind. Eng. Chem.*, **28**, 461 (1936); *Anhydrous Aluminum Chloride in Organic Chemistry*, by Charles A. Thomas (Reinhold Publishing Corp., New York).) Aluminium chloride is marketed in liquid, crystal, and anhydrous forms, and used variously in carbonizing wool and as a catalytic agent. The crystalline hydrated salt is  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ , and is soluble in water and in alcohol.

**Aluminium Sulphate** ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) constitutes the natural minerals *aluminite* (a basic salt of the composition  $\text{Al}_2\text{O}_3 \cdot \text{SO}_3 \cdot 9\text{H}_2\text{O}$ ) and the fibrous *hair-salt*. Large quantities are manufactured by dissolving the mineral *bauxite* in sulphuric acid and purifying the product from associated iron impurities which would interfere with its applications in the calico-printing, tanning, waterproofing, dyeing, paper-making, water purification and other industries. It is colourless, crystalline, soluble in water and marketed in lumps, nuts, peas and rice sizes, also large slabs.

Its use constitutes an effective and inexpensive method of changing the neutral or alkaline reaction of ordinary soil to one of acidity, and a solution of it can be used for rendering concrete floors dustless.

**Aluminium Nitrate** ( $\text{Al}(\text{NO}_3)_3$ ), in anhydrous and hydrated forms, is a white crystalline body, soluble in water, used in the textile and leather industries.

**Alums** are double sulphates, the most important of which is the so-called potash alum or ordinary alum of commerce, and they are all soluble in water. This aluminium potassium sulphate ( $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ) is a colourless, crystalline, efflorescent salt, made on a large scale by mixing the two sulphates and allowing the compound to crystallize out of solution. In a form known as "Roman alum" it is also prepared by dissolving calcined *alumstone* (*alunite*) in water, which leaves alumina undissolved; or calcined *alumstone* can be dissolved in sulphuric acid, and the solution admixed with the proper proportion of potassium sulphate and then subjected to crystallization.

There is a further process by which it can be produced from a bituminous mineral known as *alum shale*, consisting mainly of aluminium silicate with iron pyrites distributed throughout. This shale, when roasted and subsequently exposed to air and moisture, suffices to oxidize the pyrites and to form sulphuric acid, thus producing aluminium sulphate, the iron being converted into ferrous and ferric sulphates and ferric oxide, and then, when the product is lixiviated with water, the resulting solution, after addition of the requisite quantity of potassium sulphate, yields the so-called alum meal upon concentration and crystallization.

Alum is extensively used in the dyeing and calico-printing industries.

It is readily soluble in water, and when heated in the dry state melts in its own water of crystallization, which is gradually expelled by heating, and when the process is carried to a dull red heat a white porous mass of so-called *burnt alum* is left.

Ammonia alum or aluminium ammonium sulphate contains ammonium in place of the potassium of ordinary alum, and is manufactured on a considerable scale, using ammonia (as prepared in gas-works) and sulphuric acid in conjunction with the burnt alum shale already referred to.

Soda alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ ) is a crystalline soluble salt used as a mordant, also in water purification as a precipitant, and in the paper industry.

**Aluminium Acetate** ( $\text{Al}_2(\text{C}_2\text{H}_3\text{O}_2)_3$ ), or so-called "red liquor," in aqueous solution is used as a mordant in calico-printing and dyeing, also for waterproofing cloth, etc.

Other aluminium compounds of industrial use are as follows:—

The **borate** ( $2\text{Al}_2\text{O}_3 \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ), a white soluble salt used in making glass and ceramics; the **fluoride** ( $\text{Al}_2\text{F}_6 \cdot 7\text{H}_2\text{O}$ ) with small amounts of sulphuric acid for moth-proofing woollen goods; and the **phosphate** ( $\text{AlPO}_4$ ) (an insoluble compound) used in ceramics.

Aluminium **resinate**, when freshly prepared by heating aluminium hydroxide and rosin, is soluble in ether, benzene, and carbon tetrachloride, and is used in the sizing of paper. The **stearate** ( $\text{Al}(\text{C}_{18}\text{H}_{35}\text{O}_2)_3$ ) is extensively used in the oil and paint trades for thickening and increasing the viscosity of oils in which it is dissolved. Its use prevents "settling" in ready-mixed paints and produces a flattening effect.

**Aluminium Silicates** — See Clays, Kaolins, and Sillimanite.

**ALUMINIUM BRONZES** — Copper-base alloys containing about 4 to 13 per cent. aluminium and other elements such as iron, manganese, and nickel, while silicon, tin, and zinc are more rarely used. These alloys, resembling gold in appearance, combine the strength and ductility of medium-carbon steel with a high resistance to corrosion. (See *Metals*, Vol. II, by H. Carpenter and J. M. Robertson (Oxford University Press), and other books listed under Physical Metallurgy.)

**ALUMINITE** — See Aluminium Sulphate.

**"ALUMINO-FERRIC"** — A proprietary mixture of crude sulphates of iron and aluminium used as a precipitating and clarifying agent in the treatment of sewage and refuse liquids.

**ALUMS** — See Aluminium, alums.

**"ALUNDUM"** — See Abrasives.

**ALUNITE** or **ALUMSTONE** — A natural, greyish, hydrated basic potassium alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ ), of sp. gr. 2.83, found at Tolfa and elsewhere in Italy, also in Utah, where it is roasted to make sulphuric acid and yield alumina and potash. The calcined mineral, upon lixiviation with water, dissolves the potassium alum, leaving the other alumina undissolved.

**Am** — A symbol used for amyl ( $\text{C}_5\text{H}_{11}$ ).

**AMAGAT'S LAW** — See Gas Laws.

**AMALGAMS** — The name given to combinations of other metals with mercury. Gold and lead, for example, are both somewhat easily dissolved by liquid mercury in varying proportions, and while, in all probability, some of these products are definite compounds, most such combinations are probably mere mixtures or solutions. The potassium and sodium amalgams decompose water, with evolution of hydrogen, and are frequently used as reducing agents. Amalgams composed of 25 per cent. zinc, 25 per cent. tin, and 50 per cent. mercury, as also amalgams of cadmium and cadmium-tin, are used as dental cements, and the first-named one in the construction of electrical machines. Amalgams of gold and copper are also used by dentists as stoppings for teeth, and tin amalgam is employed for silvering mirrors. Of the silver-tin alloys,  $\text{Ag}_3\text{Sn}$  is stated to take up the maximum amount of mercury. There is a native amalgam of mercury and silver in which the proportion of silver ranges from 27.5 to 95.8 per cent., and a native gold amalgam containing from 39 to 42.6 per cent. is found in California and Colorado.

**AMATOL** — See Explosives.

**AMBER (Succinite and Gedanite)** ( $\text{C}_{10}\text{H}_8\text{O}$ ) — The composition of the two forms, succinite and gedanite, is very similar. It is a yellow, resin-like, combustible substance, of vegetable origin, found upon some sea-shores, including the Prussian coast, and as a fossil from the extinct conifer *Pinus succinifer* (Goppert) in certain alluvial soils, but Germany possesses the most commercially profitable deposits. Its usual position is in beds of brown coal formation of lower Tertiary Age. It becomes electrified by friction, and shows a strong fluorescence when illuminated by ultra-violet light. It finds use to some extent in the preparation of amber varnishes and amber spirit-varnishes. It contains from 3 to 4 per cent. succinic acid; yields by destructive distillation so-called amber oil, of b.p.  $130^\circ$  to  $140^\circ\text{C}$ .; sp. gr. from 0.915 to 0.975; containing some terpenes, but consisting mainly of phenols, and is used in varnish making. Values for genuine oil of amber are given by T. T. Cocking (*Analyst*, **56**, 200 (1931)).

"Amber Resin" used in pharmacy is synonymous with Colophony (see Gums and Resins). Oil of amber was formerly obtained from amber by destructive distillation but the genuine oil is now seldom encountered. It is obtained by the distillation of various resins or as a distillate of resin oil and is a pale yellow to pale brown liquid of variable composition.

Clear moulded amber has recently been used for making containers for hydrofluoric acid and strong solutions of potassium hydroxide, also as a material for making resistant beakers, dishes, and other chemical apparatus. (See A. Eisenack, *B.C.A.*, **A**, 1930, 1549.)

"Artificial amber" is a synthetic resin of the cresol-formaldehyde type, but can be distinguished from the natural product by the stain left on it after evaporation of a little ether dropped upon it.

**AMBERGRIS** — A wax-like organic substance of sp. gr. 0.908 to 0.920, varying in colour from black to white, found as a calculus in the intestinal tract of the sperm whale, consisting of a number of glycerides of highly complex fatty acids. Lumps of it are not infrequently found floating in the sea. It assumes an ointment-like character at 60° C., melts at a higher temperature, and at 100° C. volatilizes as a white vapour. It is soluble in alcohol, oils, and alkalis, and when purified is greatly valued by perfumers on account of its fine musk-like scent. The different varieties of ambergris are described by F. R. Morrison (*B.C.A.*, B, 1930, 793). (See also Cuttle-fish.)

“**AMBEROL**” (RESINS) — See “Albertol.”

“**AMBESID**” — See Sulphanilamide.

**AMERICIUM** (Am) — Element 95, and probable atomic weight 241 (longer-lived isotopes may be found). Discovered by G. T. Seaborg, R. A. James, and A. Ghiorso in 1945, and accepted (1949) by the International Union of Chemistry. Americium was made by the decay of plutonium 241 by beta particle emission. Its half-life is about 500 years.

**AMETHOCAINE HYDROCHLORIDE** (“Anethaine,” “Decicaine,” **Tetracaine Hydrochloride**) ( $C_{15}H_{24}O_2N_2.HCl$ ) — A white, crystalline, odourless compound, being the hydrochloride of  $\beta$ -dimethylamino-ethanol-*p-n*-butylaminobenzoate; m.p. 147° to 150° C.; soluble in water and alcohol. Used in medicine and dentistry as a local anæsthetic.

**AMETHYST** — A native form of silica of sp. gr. 2.5 to 2.8 and crystal system No. 3, coloured with iron and other metallic oxides.

**AMIDES (Acid)** — Organic compounds derived from ammonia by replacement of the amino group ( $NH_2$ ) for the hydroxyl radical of the carboxylic group, thus:  $CH_3CO.OH$  (acetic acid)  $\rightarrow CH_3.CO.NH_2$  (acetamide).

**Urea** or carbamide ( $CO(NH_2)_2$ ) is the amide of carbonic acid, and is prepared by heating ammonium carbamate to 135° C.

**Acetamide** ( $CH_3.CO.NH_2$ ) is a colourless, crystalline, deliquescent body derived from acetic acid; soluble in water and alcohol, m.p. 82° C.

**Benzamide** ( $C_6H_5.CO.NH_2$ ) is a crystalline substance prepared from benzoyl chloride and ammonia; soluble in hot water and alcohol, with a m.p. of 130° C.

**Formamide** ( $H.CONH_2$ ) is a colourless, oily liquid, soluble in water and alcohol, and of sp. gr. 1.146; and when heated quickly splits up into carbon monoxide and ammonia. (See “Formamide,” by P. A. Magill (*Ind. Eng. Chem.*, **26**, 611 (1934)).)

**Succinamide** ( $CONH_2(CH_2)_2CONH_2$ ) is produced by the interaction of ammonia and ethyl succinate.

**Oxamide** ( $NH_2.CO.CO.NH_2$ ), the normal amide of oxalic acid, is a white crystalline body obtainable by distillation of ammonium oxalate or by adding ammonia to ethyl oxalate.

(See Amines and Imides.)

**AMIDO** — The group  $-\text{CONH}_2$  characteristic of amides. Formerly used for  $-\text{NH}_2$  amino radical.

**AMIDOL** — The dihydrochloride of 2, 4-diaminophenol ( $\text{C}_6\text{H}_3(\text{OH})(\text{NH}_2)_2 \cdot 2\text{HCl}$ ). It is used with sodium sulphite as a photographic developing agent. (See Diaminophenol.)

**AMIDONE** (Hoechst 10820, "Methadon," "Physeptone") ( $\text{C}_{21}\text{H}_{27}\text{ON}$ ) — A synthetic, analgesic drug, being the hydrochloride of 2-dimethyl-amino-4,4-diphenyl-*n*-heptane-5-one,  $\text{CH}_3\text{CH}_2\text{N}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{C}_6\text{H}_5)_2\text{CO}\cdot\text{C}_2\text{H}_5$ , first announced in B.I.O.S., Report No. 116, Item No. 24. It has been found to be slightly greater in analgesic potency than morphine and approximately ten times greater than pethidine. For method of manufacture, see E. M. Schultz, C. M. Robb, and J. M. Sprague, *J. Amer. Chem. Soc.*, **69**, 188 (1947); N. R. Easton, J. G. Gardner and J. R. Stevens, *ibid.*, **69**, 976 (1947); and W. R. Brode and M. W. Hill, *ibid.*, **69**, 724 (1947). For an account of the analgesic activity of related compounds, see R. H. Thorp, E. Walton, and P. Ofner, *Nature* (Lond.), **159**, 679 (1947); *ibid.*, **160**, 605 (1947). By international agreement, amidone and its preparations have been included in the schedule of Dangerous Drugs.

**AMIDOPYRINE** ("Pyramidon") ( $\text{C}_{13}\text{H}_{17}\text{ON}_3$ ) — A white powder, having the formula, 4-dimethylamino-1-phenyl-2,3-dimethyl-5-pyrazolone, m.p.  $107^\circ$  to  $109^\circ\text{C}$ ., soluble about 1 in 18 of water and 1 in 2 of alcohol (95 per cent.); used in medicine as an antipyretic and analgesic. It may be prepared by addition of potassium or sodium nitrite to a concentrated solution of phenazone in dilute acetic acid, followed by reduction with zinc dust and acetic acid in alcoholic solution to aminophenazone which is then methylated by use of methyl iodide dissolved in methyl alcohol in the presence of potassium hydroxide.

**AMINACRINE HYDROCHLORIDE** (Acramine Yellow) ( $\text{C}_{13}\text{H}_{10}\text{N}_2\cdot\text{HCl}$ ,  $\text{H}_2\text{O}$ ) — A pale yellow, crystalline compound, being the hydrochloride of 9-aminoacridine; slightly soluble in water yielding a yellow fluorescent solution; soluble in alcohol and glycerin. It is used in medicine as an antiseptic and is preferred to acriflavine and proflavine as it is non-staining.

**AMINATION** — The process by which the amino group ( $\text{NH}_2$ ) is introduced into an organic compound. The following methods are most generally employed:

(1) The interaction of halogen compounds with ammonia, *e.g.*, ethyl iodide heated under pressure with ammonia yields a mixture of ethylamine, diethylamine, triethylamine, and tetraethyl ammonium iodide. The fact that mixtures are usually produced is the disadvantage of this method. Aniline is made by the reaction of 1 mole of chlorobenzene and 4 to 6 moles of ammonia under pressure of 60 atmospheres at an elevated temperature of about  $200^\circ\text{C}$ . in the presence of a catalyst consisting of cuprous oxide and chloride.

(2) The reduction of nitro compounds, *e.g.*, aniline is produced from nitrobenzene by iron and hydrochloric acid.

(3) The conversion of acid amides to amines by the method of Hofmann. This consists in treating the amide with bromine and sodium hydroxide. The product is a primary amine, free from secondary and tertiary amines. Example, phthalimide yields anthranilic acid, a valuable intermediate stage in the synthesis of indigotin.

(4) The reduction of nitriles, *e.g.*, adiponitrile, on reduction, yields hexamethylenediamine, one of the components of nylon.

(5) The reduction of oximes, *e.g.*, cyclopentanone oxime yields cyclopentylamine.

(6) Amines of the naphthalene series may be obtained from the corresponding naphthols by the Bucherer reaction, consisting of heating with ammonium sulphite or bisulphite under pressure.

Many other methods are available, but most of them are used only in special cases. Furthermore, many of the reduction reactions, once performed with metals and mineral acids, are now carried out by means of catalytic hydrogenation, either at atmospheric pressure, or under greater pressure in an autoclave. The yields are often better as under the proper conditions fewer by-products are formed.

(See *A Textbook of Practical Organic Chemistry*, by A. Vogel (Longmans, Green and Co., London); *Unit Processes in Organic Synthesis*, by P. H. Groggins (McGraw-Hill Book Co., New York); also Aniline, Hydrogenation, Indigo, and Nylon.)

#### AMINES (Nitrogen or Ammonia Bases of the Alkyl and Aryl Radicals) —

Substances derived from ammonia, but distinct from the so-called acid amides. The hydrogen atoms of ammonia are replaced by one, two, or three alkyl or aryl groups, forming respectively primary, secondary, and tertiary amines. They constitute an important class of chemical bodies intimately connected with the alkaloidal bases or alkaloids. The volatile amines have a more or less ammoniacal odour, produce white clouds with acid vapour as does ammonia, and all except tertiary aryl amines combine with hydrochloric and other acids to form salts. Like many of the alkaloids, they yield double platinum chlorides. When they contain different radicals, as, for example, methylpropylamine ( $\text{NH}(\text{CH}_3)(\text{C}_3\text{H}_7)$ ), they are described as *mixed* amines.

**Methylamine** ( $\text{CH}_3\text{NH}_2$ ) is found amongst the gaseous products of bone distillation and many decompositions of alkaloidal bodies by barium hydrate. It is manufactured by the reduction of nitromethane ( $\text{CH}_3\text{NO}_2$ ), and by reaction of methanol and ammonia. It is strongly basic, very soluble in water, and possesses a mixed ammoniacal and fish-like odour.

**Trimethylamine** ( $(\text{CH}_3)_3\text{N}$ ) (sp. gr. 0.662) is found in nature in several plants and well known as a constituent of herring brine. It can be obtained as a colourless liquefied gas of fishy ammoniacal odour, soluble in water, alcohol, and ether, and can be prepared by the interaction of methyl iodide and ammonia. It is met with in commerce in solutions of 10 and 33 per cent. strength respectively.

See "New Aliphatic Amines," by A. L. Wilson (*Ind. Eng. Chem.*, **27**, 867 (1935)) in which there are described ethylenediamine, propylenediamine, triethylenetetramine, morpholine, morpholine ethanol, and

morpholine ethyl ether; and for methods of preparation see *Organic Preparations*, by C. Weygand (Interscience Publishers, New York).

The table below shows the relationship between the primary amines :

Name	Formula	Boiling-point, °C.
Methylamine .. ..	$\text{CH}_3\cdot\text{NH}_2$	Below 0
Ethylamine .. ..	$\text{C}_2\text{H}_5\cdot\text{NH}_2$	18.7
Propylamine .. ..	$\text{C}_3\text{H}_7\cdot\text{NH}_2$	49.7
Butylamine .. ..	$\text{C}_4\text{H}_9\cdot\text{NH}_2$	69.0
Octylamine .. ..	$\text{C}_5\text{H}_{11}\cdot\text{NH}_2$	180.0

The secondary and tertiary amines corresponding to the above and their relationships are illustrated by the following table :

Name	Formula	Boiling-point, °C.
Dimethylamine .. ..	$(\text{CH}_3)_2\text{NH}$	8.5
Diethylamine .. ..	$(\text{C}_2\text{H}_5)_2\text{NH}$	57.5
Trimethylamine .. ..	$(\text{CH}_3)_3\text{N}$	4
Triethylamine .. ..	$(\text{C}_2\text{H}_5)_3\text{N}$	96

The basicity of the types of amines is shown in the following table :

Alkyl Amine	Formula	Basicity Ionization Constant
Primary-Methyl .. ..	$\text{CH}_3\cdot\text{NH}_2$	$5 \times 10^{-4}$
Secondary-Methyl .. ..	$(\text{CH}_3)_2\text{NH}$	$7 \times 10^{-4}$
Tertiary-Methyl .. ..	$(\text{CH}_3)_3\text{N}$	$7 \times 10^{-5}$
Quaternary-Methyl ammonium hydroxide	$(\text{CH}_3)_4\text{NOH}$	Strong base, like NaOH
Ammonium hydroxide .. (For comparison)	$\text{H}_4\text{NOH}$	$2 \times 10^{-5}$

Aryl Amine	Name	Formula	Melting-point °C.	Boiling-point °C.	Density	Basicity Ionization Constant
Primary-Phenyl	Aniline	$\text{C}_6\text{H}_5\cdot\text{NH}_2$	-6.2	184.4	1.022	$5 \times 10^{-10}$
Secondary-Phenyl	Diphenylamine	$(\text{C}_6\text{H}_5)_2\text{NH}$	53	302	1.16	$1 \times 10^{-13}$
Tertiary-Phenyl	Triphenylamine	$(\text{C}_6\text{H}_5)_3\text{N}$	126.5	365	0.77	No basic properties

**AMINO** — A prefix indicative of the presence of an amino group ( $\text{NH}_2$ ) in compounds. (See Amines and Amino-acids)

**AMINOACETIC ACID** — See Glycine.

**AMINO-ACIDS** — Organic acids having one or more amino ( $-\text{NH}_2$ ) groups as part of the molecule. The amino-acids are the “building stones” of the proteins, and as such are of great importance in all plant and animal life. The simplest amino-acid is glycine ( $\text{CH}_2(\text{NH}_2)\text{COOH}$ ), also called aminoacetic acid and glycoll (see Glycine). Because they contain an acid radical ( $-\text{COOH}$ ) and a basic radical ( $-\text{NH}_2$ ), amino-acids readily combine with each other to form complex molecules with high molecular weights—the proteins.

Most of the amino-acids are aliphatic, but several contain ring structures. Examples of these are phenylalanine and tyrosine. Others contain sulphur (cystine) and iodine (thyroxine). It has been found that certain amino-acids are essential to animal life: not all of these are found in every protein. The amount and kind of the amino-acids in a protein may be determined by breaking the protein molecule into its constituent amino-acids by hydrolysis. Amino-acids are important as constituents, through the peptide linkage ( $-\text{CO.NH}-$ ), of proteins that occur in plants and animals, and the naturally occurring amino-acids have the amino group in the *alpha* position on the carbon atom next to the  $-\text{COOH}$  group thus, alanine  $\text{CH}_3.\text{CH}_2\text{NH}_2.\text{COOH}$ . (See *The Biochemistry of the Amino Acids*, by Mitchell and Hamilton (Reinhold Publishing Corp., New York); *The Chemistry of the Amino Acids and Proteins*, by C. L. A. Schmidt (C. C. Thomas, Baltimore); *Outline of the Amino Acids and Proteins*, by M. Sahyun (Reinhold Publishing Corp., New York); Arginine, Aspartic Acid, Cysteine, Cystine, Glutamic Acid, Glycine, Histidine, Leucine, Polypeptides, Proteins, and Tyrosine.)

**AMINOAZOBENZENE** ( $\text{NH}_2.\text{C}_6\text{H}_4.\text{N}:\text{N}.\text{C}_6\text{H}_5$ ) — The parent substance of the chrysoidines (dyes).

**AMINO BENZOIC ACIDS** ( $\text{NH}_2.\text{C}_6\text{H}_4.\text{COOH}$ ) — All three of these are amphoteric and soluble in water. The ortho acid is anthranilic acid (see same). The meta acid is also used in the dye and perfume industries. It melts at  $174^\circ\text{C}$ . The para acid melts at  $187^\circ\text{C}$ . and is important as an essential metabolite for certain bacteria and as an inhibitor for the sulphonamide group of drugs. (See Sulphanilamide, and Vitamins.)

**AMINODIPHENYL** — Both ortho ( $2\text{-NH}_2$ ) and para ( $4\text{-NH}_2$ ) compounds are used as intermediates for dyestuffs and allied chemicals.

**AMINOPHENOLS** ( $\text{NH}_2.\text{C}_6\text{H}_4.\text{OH}$ ) — These are obtained by reduction of nitrophenols, and are more or less unstable, but their hydrochlorides are much more stable. The ortho-, meta-, and para- varieties of aminophenol are white crystalline bodies soluble in water, alcohol, and ether, and are used in the dyestuffs industry. The para-variety is also used as a photographic developer.

**AMINOPHYLLINE** (“Cardophyllin,” Theophylline with Ethylenediamine) — A white or yellowish-white material containing about 75 per cent. of anhydrous theophylline and about 12.5 per cent. of ethylenediamine; soluble in water, insoluble in alcohol and ether; used in medicine as a cardiac and respiratory stimulant and diuretic. (See Theophylline.)

**AMINOSALICYLIC ACID** (Para-aminosalicylic Acid, "Paramisan," P.A.S.) ( $C_7H_8O_3N$ ) — A white, crystalline compound, namely, 4-amino-2-hydroxybenzoic acid; sparingly soluble in water; on heating, it decomposes and the m.p. varies according to technique. It forms a sodium salt which is freely soluble in water, and is used for the treatment of tuberculosis, either alone or in combination with streptomycin. (See J. Lehman, *Lancet*, 1, 15 (1946); Seymour, Simmonite and Oberweger, *Quart. J. Pharm.*, 21, 292 (1948); Goodacre, Mitchell and Seymour, *ibid.*, 21, 301 (1948); Venkataraman and Lewis, *J. Biol. Chem.*, 173, 641 (1948); Bray, Ryman and Thorpe, *Nature* (Lond.), 162, 64 (1948); Report of the Medical Research Council, *Brit. Med. J.*, 2, 1521 (1949); Drain *et al.*, *J. Chem. Soc.*, 1949, 1498; Seaman *et al.*, *J. Amer. Chem. Soc.*, 71, 2940 (1949).)

**"AMMATE"** — Ammonium sulphamate, used as a herbicide.

**AMMINES** — Metal-ammonium compounds, such as the cobalt- and platinum-ammonium compounds and copper-ammonium salts. Some of these compounds are very complex—for example, Erdmann's salt (ammonium tetranitrodiammine cobaltate). The number of neutral groups, such as  $NH_3$  or  $H_2O$  (each of which is a material capable of independent existence), varies from 6 to 0 for cobalt or chromium and can form a series as the following illustrates:

Ammine (ion in square brackets)	Equivalent Electrical Conductivity
$[Co(NH_3)_6]Cl_3$	410
$[Co(NH_3)_5(NO_2)]Cl_2$	240
$[Co(NH_3)_4(NO_2)_2]Cl$	95
$Co(NH_3)_3(NO_2)_3$	1.5
$K[Co(NH_3)_2(NO_2)_4]$	95
$K_2[Co(NH_3)(NO_2)_5]$	240
$K_3[Co(NO_2)_6]$	420

The neutral group may be replaced step by step by negative groups, as shown above. (See J. Newton Friend, *Textbook of Inorganic Chemistry* (Charles Griffin and Co., Ltd., London), vol. x, on *The Metal-Ammines*, by Miss M. M. J. Sutherland; and Platinum (Platinammonia Compounds).)

**AMMONAL** — See Explosives.

**AMMONIA** — See Nitrogen and Nitrogen Fixation.

**AMMONIACUM GUM** — See Gums and Resins.

**AMMONIA-OLEÏN** — See Turkey-red Oil.

**AMMONIA-SODA PROCESS** — See Sodium (Carbonate).

**AMMONIUM and its Compounds** — See Nitrogen Compounds.

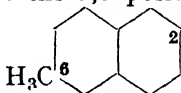
**AMOBARBITAL** — See Amylobarbitone.

**AMORPHOUS** -- Glasses and resins are not bounded by plane surfaces to give any degree of crystal symmetry and are classed as *amorphous* substances. An amorphous substance is to be regarded as a high

viscosity liquid. Amorphous solids upon being heated lose, by imperceptible gradations, their rigidity and may become as fluid as water without undergoing a definite transition point. Küster in 1894 showed that the distribution law was valid when an amorphous substance was substituted for one of the liquids.

**AMPHETAMINE** ("Benzedrine") ( $C_9H_{13}N$ ) — A colourless, mobile liquid, namely,  $\beta$ -aminopropylbenzene, having a characteristic odour and acrid taste; b.p. about  $200^\circ C.$ ; slightly soluble in water; soluble in alcohol and ether. It is used in medicine as a vasoconstrictor to relieve nasal congestion and is administered by inhalation. Amphetamine sulphate is a white, odourless substance having a bitter taste; soluble in water, slightly soluble in alcohol, insoluble in ether. It is used as a stimulant and euphoriant in the treatment of mild psychoses.

**AMPHI** — Substitutions in the 2,6 positions of naphthalene, *e.g.*, 2,6-dimethylnaphthalene,



See also Dioximes.

**AMPHIBOLE** (Uralite) — There are a great number of rock-forming members of the Amphibole group, including tremolite, glaucophane, hornblendes, etc. (See Asbestos, and Hornblende.)

**AMPHOTERIC** — Amphoteric compounds are partly of one nature and partly of the other, so that they exhibit the qualification of acting either in the acid or basic capacity; thus, aluminium hydroxide dissolves in acids forming salts and in strong basic solutions forming aluminates:  $Al(OH)_3 + 3HCl = AlCl_3 + 3H_2O$  and  $Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O$ .

**AMYGDALIN** — See Glycosides, and Almond Oil.

**AMYLACEOUS** — See Gums, Starches, and Cellulose.

**AMYLASES** — Enzyme constituents of grain. (See Beer, Diastase, Enzymes, and Starch.)

**AMYL ACETATE** ( $CH_3.COOC_5H_{11}$ ) — A colourless, liquid ester, of sp. gr. 0.866 and b.p.  $148^\circ C.$  It is almost immiscible with water, of pleasant ethereal odour, and is used in flavouring essences, the alcoholic solution being known as essence of pears. Large quantities are used as a solvent for plastics and in waterproofing processes.

**AMYL ALCOHOL** — See Alcohols, and Fusel Oil.

**AMYL BUTYRATE** ( $C_3H_7.COOC_5H_{11}$ ) — A colourless liquid ester of sp. gr. 0.859, and b.p. about  $154^\circ C.$ , prepared by distillation of a mixture of amyl alcohol and butyric acid after addition of sulphuric acid; used as a flavouring principle, and in the making of liqueurs. (See Perfumes.)

**AMYL CINNAMIC ALDEHYDE** — See Jasmine Oil.

**AMYL FORMATE** ( $\text{H.COOC}_5\text{H}_{11}$ ) is a colourless liquid ester of b.p.  $130.4^\circ\text{C}$ ., and sp. gr. 0.9018, soluble in alcohol and ether, used for flavouring; prepared in a corresponding manner to amyl butyrate from formic acid.

**AMYL NITRITE** ( $\text{C}_5\text{H}_{11}\text{O.NO}$ ) — A yellowish liquid ester, soluble in alcohol and ether, of sp. gr. at  $15^\circ\text{C}$ . of from 0.870 to 0.880, b.p.  $96^\circ\text{C}$ .; used as a stimulant inhalant in cases of *angina pectoris*; also in perfumery and making fruit essences. It is prepared by distillation from a mixture of amyl alcohol and sodium nitrite to which sulphuric acid has been added.

**AMYL SALICYLATE** ( $\text{C}_6\text{H}_4(\text{OH})(\text{COOC}_5\text{H}_{11})$ ) — A colourless or slightly yellow liquid ester of sp. gr. 1.045, and b.p. about  $270^\circ\text{C}$ ., prepared from amyl alcohol and salicylic acid in a similar way to that of the butyrate; soluble in alcohol and ether, and used in perfumery and for flavouring.

**AMYL VALERATE** (Apple Oil) ( $\text{C}_4\text{H}_9.\text{COOC}_5\text{H}_{11}$ ) — Prepared from amyl alcohol and valeric acid in a similar way to that of the butyrate; sp. gr. 0.881 and b.p.  $203.7^\circ\text{C}$ .; and used as a flavouring body.

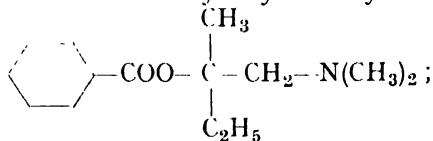
**AMYLENE** ("Pental" or Trimethylethylene) ( $(\text{CH}_3)_2\text{C}:\text{CH.CH}_3$ ) is a colourless, mobile, inflammable liquid of b.p.  $35^\circ\text{C}$ . and sp. gr. 0.666, soluble in alcohol and ether, produced from ordinary amyl alcohol by the action of zinc. A great number of isomeric amylenes are known, "Pental" being one form. (See Hydrocarbons.)

**AMYLO** — Concerning starch.

**AMYLO PROCESS** — See Alcohols.

**AMYLOBARBITONE** (Amobarbital, "Amytal") ( $\text{C}_{11}\text{H}_{18}\text{O}_3\text{N}_2$ ) — A white, crystalline, odourless substance, namely, 5-isoamyl-5-ethylbarbituric acid; very slightly soluble in water; soluble in alcohol and ether; m.p.  $153^\circ$  to  $155^\circ\text{C}$ . Used in medicine as a hypnotic and sedative. By the action of sodium ethoxide, amylobarbitone forms a white, hygroscopic sodium compound which is freely soluble in water and alcohol, and is used in medicine when a rapid effect is desired.

**AMYLOCAINE HYDROCHLORIDE** ( $\text{C}_{14}\text{H}_{21}\text{O}_2\text{N.HCl}$ ) — A synthetic local anæsthetic, being the hydrochloride of methylethyldimethylaminomethylcarbinol benzoyl ester,



soluble in water and alcohol, insoluble in ether, m.p.  $177^\circ$  to  $179^\circ\text{C}$ .

**AMYLOPSIN**, otherwise known as pancreatic diastase, is one of the enzymes contained in pancreatine, capable of converting starch into dextrin and maltose. It acts best in neutral or slightly alkaline media at a temperature of between  $30^\circ$  and  $45^\circ\text{C}$ ., and is destroyed at  $65^\circ\text{C}$ .

**AMYLOSE** — One of the two components of starch, the other being amylopectin. (See *An Introduction to the Chemistry of Carbohydrates*, by Honeyman (Clarendon Press, Oxford); also Carbohydrates, and Starch.)

**AMYLUM** — See Carbohydrates, and Starch.

**"AMYTAL"** — See Amylobarbitone.

**"ANACARDONE"** — See Nikethamide.

**"ANACOBIN"** — A proprietary name for a preparation containing the crystalline vitamin B<sub>12</sub> obtained from liver. (See Vitamins.)

**ANÆSTHETICS** — Substances which produce loss of sensation or feeling in the whole or part of the body. General anæsthetics produce lack of consciousness and involve paralysis of the whole body except the respiratory and circulatory centres. Local anæsthetics produce insensibility to pain in a localized area of the body and do not involve loss of consciousness.

Diethyl ether, called ether, is commonly used as a general anæsthetic. The modern methods of use date from the demonstration by William Morton, at the suggestion of Charles Jackson, in 1846, at the Massachusetts General Hospital.

The anæsthetic property of nitrous oxide, or "laughing gas," was discovered by Sir Humphry Davy in 1799. This gas, in admixture with oxygen, is used in dentistry and other operative procedures.

Chloroform, introduced as a general anæsthetic in 1847, has largely been replaced by safer and less toxic substances.

Ethylene, divinyl oxide (vinyl ether, "Vinesthene"), trichloroethylene ("Trilene"), and cyclopropane are other anæsthetics that have come into general use.

Soluble barbiturates such as hexobarbitone sodium ("Evipan") and thio-pentone sodium ("Pentothal") are administered by intravenous injection to produce general anæsthesia.

For local anæsthesia, cocaine has been replaced very largely by derivatives of amino-alcohols, such as procaine hydrochloride. Compounds of this type are also used for spinal anæsthesia.

A survey of modern anæsthetics by N. L. Allport appears in *Ind. Chem.*, **14**, 115, 187 (1938), in which there is given an important list of products sold under proprietary names. The clinical application of chemical contributions in this field is discussed by J. S. Lundy, *Ind. Eng. Chem.*, **28**, 1031 (1936). See also "Chemical and Pharmaceutical Aspects of Anæsthesia," by H. Davis (*Pharm. J.*, **104**, 167, 187 (1947)); and *Anæsthetics*, by H. B. Nisbet (Royal Institute of Chemistry, Lectures, Monographs, and Reports, No. 3 (1949)).

**ANALCITE** — A zeolitic mineral of constitution (Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O, 4SiO<sub>2</sub>, 2H<sub>2</sub>O), of crystal system No. 1, and sp. gr. 2.22.

**ANALGESINE** — See Phenazone.

**ANALYTICAL CHEMISTRY** covers all those operations which are performed in order to determine the constituents of a substance, and is

divided into *qualitative* and *quantitative* analysis. Qualitative analysis deals with the methods for determining the nature of the constituents while quantitative analysis is applied qualitative analysis and deals with the methods for determining the percentage of each constituent present in the substance.

Qualitative analysis is based upon subjecting the substance to a series of systematic physical and chemical tests until there is produced a compound with distinctive features which can be recognized. For qualitative analysis only those changes are applicable that are perceptible to our senses, such as the formation of a precipitate ; a change in colour ; the formation of a gas ; the dissolving of a precipitate.

A systematic approach and an unbiased observation are most necessary to correctly interpret the results and to identify the constituents by an analysis. The systematic analysis should include :

- (1) Description of the sample.
- (2) Solubility in various solvents.
- (3) Test for fusibility.
- (4) Test for volatility.
- (5) Test for oxidation and reduction :
  - (a) borax bead or phosphate bead,
  - (b) charcoal reduction.
- (6) Test for flame colour.
- (7) Systematic analysis for functional groups.

All quantitative analysis is based upon the analytical balance. An understanding of the workings of the balance, its proper operation and care, and the calibration of weights become paramount items in developing the proper technique in quantitative analysis. The subject is generally divided into the following methods :

(1) **Gravimetric analysis** requires that the constituent sought be separated from the other components in a weighable form, such as, by precipitation, electrodeposition, or volatilization.

Before a precipitate can be successfully used in analysis it must be quantitatively insoluble, have favourable physical properties to allow it to be filtered and washed free from soluble impurities, and the precipitate must be a pure substance of definite chemical composition or must be convertible into a pure substance of definite composition in order that the weight of the constituent sought may be calculated by use of the appropriate chemical factor. For example, magnesium can be precipitated as  $\text{MgNH}_4\text{PO}_4$  and ignited to  $\text{Mg}_2\text{P}_2\text{O}_7$  and weighed.

By using the chemical factor  $\frac{2\text{MgO}}{\text{Mg}_2\text{P}_2\text{O}_7}$  we can determine the percentage of the weighed precipitate that is MgO.

Copper, lead, nickel, and other metals can be removed from a solution in a pure form by proper control of voltage and acidity by electro-deposition on weighed inert electrodes which can be dried, reweighed, and the gain in weight determined.

A volatile component can be liberated from the sample, but it must

be reabsorbed by the proper reagent which is specific for the volatile component sought.

(2) **Volumetric analysis** is a method of analysis wherein a weighed sample is determined by means of titrating against a solution of known concentration which will undergo a definite chemical reaction with the constituent sought. Titration is the measurement of the amount of standard solution required for reaction with the sample.

In order to determine the amount of constituent present volumetrically there must be a well-defined, complete reaction between the standard and the sample, and an indicator to detect the point when equivalent amounts of standard and sample constituent are present. A reaction to qualify for use in volumetric analysis must satisfy the following requirements: it must be rapid (mostly ionic); there must be only one reaction which can be expressed by a chemical equation; the reaction must be complete; there must be some marked change in some property of the solution at the equivalence point; an indicator must be available which will make visible the above-mentioned property change.

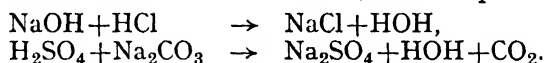
The fundamental equation for calculating the percentage composition by volumetric analysis is:

$$\frac{V \times N \times \text{milliequivalent weight of constituent}}{\text{weight of sample}} \times 100 = \%,$$

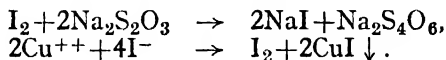
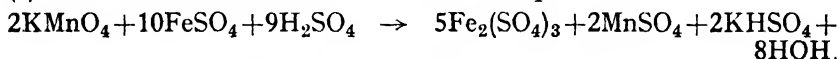
where  $V$  = millilitres of standard used, and  $N$  = normality of standard solution.

There are three fundamental types of reactions that can be utilized in volumetric analysis when they meet the above requirements:

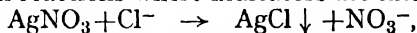
(a) Acid-Base or neutralization reactions, for example:



(b) Oxidation-Reduction reactions, for example:



(c) Precipitation reactions where indicators are known, for example:



using chromate or dichlorofluorescein as indicator.

(3) **Electrometric titrations** — These are of the same type as in volumetric analysis except that the equivalent point is determined by means of an electrometric observation. For example, in an acid-base titration there is a sharp change in  $pH$  as the equivalence point is reached and this is shown in the E.M.F. of the cell used in the titration.

(4) **Colorimetric analysis** (visual or electrophotometric) — By comparing the intensity of transmitted light (or measuring the amount of absorbed light) of a given colour with a standard and with a known solution of the sample. In this case the standard must contain the

same component that produces the colour in the sample, for example, manganese, titanium, ammonia.

(5) **Special methods of analysis** comprise the following :

- (a) Gas analysis,
- (b) Polariscope readings,
- (c) Emission and absorption spectra,
- (d) Refractive index readings,
- (e) Polarizing microscopy,
- (f) Polarography,
- (g) Mass spectroscopy,
- (h) Spectroscopy,
- (j) Chromatography.

*Analytical Chemistry*, published by American Chemical Society, is devoted to this field of chemistry, as is also *The Analyst*, published by W. Heffer and Sons, Cambridge, England.

**ANASTASE (Anatase)** — Mineral titanium oxide ( $\text{TiO}_2$ ), of crystal system No. 2, and sp. gr. 3.75 to 4.0. (See Titanium.)

**ANDALUSITE**—A mineral trimorphous form of crystallized aluminium silicate ( $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ ), found in Andalusia (Spain) and elsewhere ; of sp. gr. 3 to 3.3 and crystal system No. 4 ; of some value as a refractory and for making porcelain cores of sparking plugs. (See Sillimanite.)

**ANDIROBA OIL (Crabwood Oil)** — Obtained from the nuts of the andiroba tree of Brazil. The nuts yield about 64 per cent. of oil. The oil is non-drying, and is used in soap making.

**ANDROGENS** — A general term applied to the hormones which cause the development of secondary male characteristics. (See Androsterone, and Testosterone.)

**ANDROSTERONE** — A steroidal substance considered to be one of the male sex hormones. (See Testosterone.)

**ANEMOMETERS** — Instruments for measuring the direction, velocity, and force of the wind. Fletcher's anemometer is one designed to measure the speed of flue gases. (See *Chemical Engineering*, by G. E. Davis, i., 193, Davis Bros., Manchester.)

“ **ANETHAINE** ” — See Amethocaine Hydrochloride.

**ANETHOLE** ( $\text{C}_9\text{H}_4\cdot\text{C}_3\text{H}_5(\text{OCH}_3)$ ) — The principal constituent of Aniseed oil, namely, *p*-methoxypropenylbenzene ; m.p.  $21^\circ\text{C}$ . ; b.p.  $235^\circ\text{C}$ . ; sp. gr. 0.983 to 0.988 at  $15^\circ\text{C}$ . ; soluble in alcohol and ether. It is also obtained from fennel (*Foeniculum vulgare*) and tarragon (*Artemisia dracunculus*). Two dimerides of anethole are known, see Goodall and Haworth, *J.C.S.*, 1930, 2482. (See Aniseed Oil, and Aubepine.)

**ANEURINE HYDROCHLORIDE (Aneurine Chloride Hydrochloride, Vitamin B<sub>1</sub>)** — See Vitamins.

**ANGELICA** (*Archangelica officinalis*) — A plant, parts of which are used for flavouring purposes and in the rectification and compounding of gin. The root contains angelic acid ( $\text{C}_5\text{H}_8\text{O}_2$ ), a crystalline, colourless substance, m.p.  $45^\circ\text{C}$ . ; used in medicine as a stimulant. The German

and Japanese root oils, as also that distilled from the seeds (the yield being 1.15 per cent. and sp. gr. 0.86 to 0.89), are all used in medicine and the preparation of liqueurs. The distilled oil contains phellandrene and valeric acid.

**ANGLESITE** — Native lead sulphate, of crystal system No. 4, and sp. gr. about 6, found in Spain, North America, and Cumberland, probably produced by the oxidation of galena (lead sulphide).

**"ANGOSTURA" BITTERS** — A proprietary form of aromatic bitters, obtained from the bark of *Cusparia*, N. O. Rutaceae. The bitter principle of the bark was originally extracted by Capuchin Friars in Venezuela, and was shipped from the town of Angostura, later named Ciudad Bolivar. The bark itself is said to contain several alkaloids, including cusparine and galapine. It yields an oil of sp. gr. 0.93 to 0.96 soluble in alcohol and containing cadinene.

**ÅNGSTRÖM UNITS** — See Wave-Lengths.

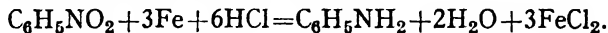
**ANHYDRIDES**—Substances resulting from the abstraction of the elements of water from other substances. For instance, the metallic hydroxides (of which potassium hydroxide (KOH) is illustrative) give the corresponding oxides or anhydrides by deprivation of water; thus,  $2\text{KOH}=\text{K}_2\text{O}+\text{H}_2\text{O}$ . Again, acetic anhydride is similarly obtained from acetic acid; thus  $2\text{CH}_3\cdot\text{COOH}=(\text{CH}_3\cdot\text{CO})_2\text{O}+\text{H}_2\text{O}$ . In a sense also cymene ( $\text{C}_{10}\text{H}_{14}$ ) may be regarded as the anhydride of camphor, as the latter by distillation with phosphoric anhydride yields cymene,  $\text{C}_{10}\text{H}_{16}\text{O}=\text{C}_{10}\text{H}_{14}+\text{H}_2\text{O}$ .

**"ANHYDRONE"** — A proprietary form of magnesium perchlorate, used as a water absorbent in quantitative analysis.

**ANHYDROUS** — Devoid of water as a constituent.

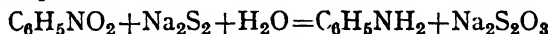
**ANILIDES** — Compounds such as acetanilide, formed from aromatic amines by substitution of acyl groups for hydrogen in the amino group.

**ANILINE (Aminobenzene, Phenylamine)** ( $\text{C}_6\text{H}_5\cdot\text{NH}_2$ ) is an arylamine being a derivative of ammonia, one hydrogen atom being replaced by the phenyl group, and is manufactured by acting on nitrobenzene with iron filings and hydrochloric acid or ferrous chloride, and subsequently distilling with steam after the addition of lime. The following equation expresses the initial chemical change:



The small amount of ferrous chloride acts catalytically in facilitating the reduction of nitrobenzene by iron and water. Aniline and hydrated  $\text{Fe}_3\text{O}_4$  are the two main products.

It can also be prepared from nitrobenzene by reduction, using sodium disulphide:



In a later modification the reduction of nitrobenzene is effected by passing its vapour, mixed with hydrogen gas, over a catalyst at an K.C.E.—3

appropriate temperature, and another process for its preparation is from chlorobenzene and ammonia. (See Amination.)

Aniline is an oily, colourless liquid of peculiar odour, which darkens on exposure to air, and finally dries up into a resin-like mass. The physical constants of pure aniline, as recently determined, are as follows: f.p.,  $6.24^{\circ}\text{C.}$ ; b.p.,  $184.32^{\circ}$  to  $184.39^{\circ}\text{C.}$ ; sp. gr., 1.0268; and ref. ind. at  $20^{\circ}\text{C.}$ , 1.5850. It is soluble 1 in 31 parts water, also in alcohol and ether, and behaves as a base like ammonia, but is weaker, poisonous, and forms a number of salts, including aniline hydrochloride ( $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$ ). Aniline oil gives off a poisonous vapour, and is the base or starting-point from which a great number of other "intermediates" for dyes are prepared, including dimethylaniline and diethylaniline, and these yield in turn many so-called basic dyes, such as methyl violet, methylene blue, and malachite green. By boiling aniline with glacial acetic acid, acetanilide ( $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{COCH}_3$ ) is produced, otherwise known under the medicinal name of "antifebrine." (See Acetanilide.)

Aniline blue (phenylrosaniline) is prepared from aniline, magenta base, and benzoic acid.

(See *Aniline and its Derivatives*, by P. H. Groggins (Chapman and Hall, Ltd., London).)

**ANILINE BLACK** — A dye for cotton and other textiles produced by oxidation of aniline on the fabrics. (See J. L. Hankey, *Chem. and Ind.*, **89**, 1027 (1930); and Dyes.)

**ANILINE POINT** — The temperature at which a cloud forms when a solution of equal volumes of a hydrocarbon and aniline is cooled. Benzenoid hydrocarbons form a clear solution at temperatures as low as  $-30^{\circ}\text{C.}$ , cycloparaffins at  $30^{\circ}$  to  $35^{\circ}\text{C.}$ , and paraffins at  $70^{\circ}$  to  $75^{\circ}\text{C.}$  The aniline points of thirty synthetic hydrocarbons, which are alkyl derivatives of benzene, naphthalene, diphenyl, are given in *Ind. Eng. Chem.*, **28**, 972 (1936); and of aromatic hydrocarbons in *Ind. Eng. Chem.*, **26**, 477 (1934).

**ANILINE SALT** — Aniline hydrochloride ( $\text{C}_6\text{H}_5\text{NH}_2\cdot\text{HCl}$ ), which crystallizes in large colourless plates, and can be distilled without change; m.p.  $198^{\circ}\text{C.}$ , b.p.  $245^{\circ}\text{C.}$ ; soluble in water and in alcohol, but insoluble in ether. It is used in the dyeing industry.

**ANIME RESIN (or Gum)** — See Gums and Resins (Copal).

**ANIONS** — See Electricity (Electrochemical Aspects).

**ANISALDEHYDE** — See Perfumery.

**ANISEED OIL (Anise Oil)** — A yellowish, syrupy volatile oil obtained by distillation from the seeds of *Pimpinella Anisum* (Anise fruit) which is cultivated in Spain, Asiatic Turkey and Russia, or from the seed of *Illicium verum* (Star Anise) which is indigenous to China. It possesses a characteristic, aromatic odour and taste and contains from 80 to 90 per cent of anethole. Aniseed oil solidifies at  $15^{\circ}\text{C.}$ ; sp. gr. 0.980 to

0.994 at 15° C. ; ref. ind. 1.553 to 1.560 at 20° C. ; soluble in alcohol and ether ; used as a flavouring agent and carminative. (See Anethole, and Aubepine.)

**ANKERITES (Mineral Parts of Coal)** — See Coal.

**ANNATTO** — A fugitive colouring matter made from the seeds of the *Bixa orellano*, cultivated in Guiana, St. Domingo, and the Indies. It dissolves in alcohol to an orange-red colour, and contains a crystalline yellow substance named bixin, which in the presence of alkalis absorbs oxygen and turns red. It is used in dyeing and wood-staining, also for colouring butter, cheese, etc.

**ANODE** — See Electricity (Electrochemical Aspects).

**ANORTHITE** ( $\text{CaAl}_2\text{Si}_2\text{O}_8$ ) — A mineral compound silicate of aluminium and calcium of sp. gr. 2.7 and crystal system No. 6.

**"ANTABUSE"** — The Danish proprietary name for tetraethylthiuram disulphide, administered in the treatment of chronic alcoholism. Following the administration of the drug, patients react abnormally to relatively small amounts of alcohol, probably due to interference with the oxidation of the alcohol in the body resulting in a high concentration of acetaldehyde. The symptoms are characterised by a feeling of heat in the face, flushing of the face and upper part of the body, throbbing of the head and neck and an accelerated pulse. If larger amounts of alcohol are taken after "Antabuse," nausea, copious vomiting and a fall in blood pressure result. The symptoms may last from 30 minutes to several hours but after a few hours sleep, the patient feels well again (see R. G. Bell and H. W. Smith in *Canad. Med. Ass. J.*, **60**, 286 (1949)).

**"ANTHISAN"** ("Neo-Antergan," Pyranisamine Maleate, Mepyramine Maleate) ( $\text{C}_{17}\text{H}_{23}\text{ON}_3$ ) — A complex organic compound being the acid maleate of N-dimethyl-amino-N-*p*-methoxybenzyl- $\alpha$ -aminopyridine. It is one of a series of drugs which antagonize the action of histamine and is used in medicine for the treatment of a number of allergic conditions such as serum sickness and hay-fever.

**ANTHOCYANINS** — See Plant Colouring Matters.

**ANTHOXANTHENES (Anthoxanthins)** — See Plant Colouring Matters.

**ANTHRACENE** ( $\text{C}_{14}\text{H}_{10}$  or  $\text{C}_6\text{H}_4(\text{CH})_2\text{C}_6\text{H}_4$ ) — A product of the destructive distillation of coal, present in coal-tar to the extent of from  $\frac{1}{4}$  to nearly  $\frac{1}{2}$  per cent. In the pure state it is a colourless crystalline body, and exhibits a fine blue fluorescence. It is obtained from the anthracene oil, which forms about 12 to 17 per cent. of the tar and distils over between 270° and 300° C. Upon cooling, the crystals of anthracene are separated from the oily mother-liquor by pressing and centrifugalizing. This crude product, containing about 40 to 45 per cent. anthracene, is further purified from naphthalene, phenanthrene, crysene, carbazole, and other associated bodies, by exposure to steam in a hydraulic press, after which it is washed with a mixture of solvent naphtha mixed with pyridine bases. In this way a product containing about 90 per cent. anthracene can be obtained. By dissolving the crude article in

furfural at an elevated temperature and subsequent cooling, anthracene of excellent quality for direct oxidation to anthraquinone separates out. Chemically pure anthracene is obtained by grinding up the crude substance with caustic potash and lime, and redistillation, the product being finally washed with solvent and sublimed.

Anthracene, m.p.  $218^{\circ}\text{C.}$ , b.p.  $340^{\circ}\text{C.}$ , is used for making anthraquinone and various aniline colours, especially Turkey red. (See *Anthracene and Anthraquinone*, by E. de Barry Barnett (Baillière, Tindall and Cox, London); and Alizarin.)

**ANTHRACITE** — See Coal.

**ANTHRANILIC ACID** (*o*-Aminobenzoic Acid) ( $\text{C}_6\text{H}_4(\text{NH}_2)(\text{COOH})$ ) — A yellow crystalline salt, m.p.  $144^{\circ}\text{C.}$ , soluble in water, alcohol, and ether; used in the dye industry. (See Indigo.)

**ANTHRALIN** — See Dithranol.

**ANTHRAQUINONE** ( $\text{C}_6\text{H}_4(\text{CO})_2\text{C}_6\text{H}_4$ ) — A product of the oxidation of anthracene; also manufactured by the catalytic oxidation of naphthalene to phthalic anhydride by Gibb's vapour-phase process and the condensation of this anhydride with benzene in presence of aluminium chloride. It crystallizes in yellow needles, m.p.,  $285^{\circ}\text{C.}$ , is readily sublimable, soluble in alcohol, ether, and acetone, and used in the dyestuffs industry.

**ANTIBIOTICS** — Substances produced by both vegetable and animal organisms which have the power of inhibiting the growth of or destroying bacteria and other micro-organisms. The production of such substances was first recognized by Pasteur and a review of early literature on the subject has been given by H. W. Florey, *Brit. Med. J.*, **2**, 635 (1945). Antibiotics are generally specific in their action, each having a characteristic antimicrobial spectrum (see Waksman, *Mycologia*, **39**, 568 (1947)). The most important therapeutic developments in this field have been the discovery of penicillin and the subsequent development of streptomycin, chloromycetin, and aureomycin for use in medicine. For a comprehensive review of antibiotic research, see Waksman and Schatz, *J. Amer. Pharm. Assoc.*, **34**, 273 (1945); *Ann. Rep. Soc. Chem. Ind.*, **33**, 603 (1948); P. Regna, *Chem. et Ind.*, **18**, 275 (1948); *Microbial Antagonisms and Antibiotic Substances*, by Waksman (The Commonwealth Fund, 1947); *Penicillin*, edited by Sir Alexander Fleming (Butterworth and Co., London); *Antibiotics*, by George W. Irving, Jr., and H. T. Herrick (Chemical Publishing Co., Booklyn); and *Antibiotics*, by R. Pratt and Jean Dufrenoy (J. B. Lippincott Co., Philadelphia). (See Aureomycin, Bacillosporin, Chloromycetin, Gramicidin, Penicillin, Polymixin, Streptomycin, and Tyrocidin.)

**ANTIBODIES** — Substances produced in the blood as a natural defence mechanism when foreign proteins (antigens) are introduced into the blood stream. Each antibody is specific for the corresponding antigen and may react with it in one of several ways. Antibodies are known as agglutinins, precipitins, antitoxins, and lysins according to the type of reaction which they undergo with the corresponding antigens. (See Bacteria, and Toxins.)

**ANTICHLOR** — A term used by bleachers in respect of chemicals (such as sodium sulphite and sodium thiosulphate), employed for the purpose of obviating any deleterious after-effects of the action of chlorine preparations used in bleaching operations by removing any excess chlorine.

**ANTIFEBRINE** — See Acetanilide.

**ANTI-FOULING COMPOSITIONS** — See Paints.

**ANTI-FREEZES** — The lowering of the freezing point of water is accomplished by the addition of a solute, principally methanol, ethanol, or ethylene glycol in anti-freezes. A solution of 50 per cent. ethanol-50 per cent. water by weight freezes at  $-37^{\circ}\text{C}$ . ( $-34^{\circ}\text{F}$ .) (of sp. gr. 0.910); one of 50 per cent. ethylene glycol-50 per cent. water at  $-34^{\circ}\text{C}$ . ( $-29^{\circ}\text{F}$ .) (of sp. gr. 1.067). To prevent corrosion of the container, *e.g.*, radiator, **inhibitors** are added to commercial anti-freezes. Inhibitors are of two types, namely, inorganic salts, such as alkali borates, chromates, molybdates, nitrates, phosphates, and tungstates, and organic materials, such as mineral and vegetable oils and their sulphonated products, soaps, and amines. Foaming and seeping of non-volatile solutes, *e.g.*, ethylene glycol, and glycerol, are counteracted by adding alkyl lactates, dibutyl phthalate, ethyl oleate, phenyl stearate, calcium acetate, amyl alcohol, or castor-oil soap.

**ANTIGENS** -- Substances which when injected into the blood cause the formation of specific antibodies. (See Bacteria, and Toxins.)

**ANTI-HISTAMINES** -- A group of drugs which exert their effect by blocking the tissue receptors for histamine. They include derivatives of ethylenediamine, phenothiazine, and piperazine, and are used in medicine for the treatment of allergic conditions such as urticaria, serum sickness, hay-fever, and asthma. They have also been advocated for the treatment of the common cold, but their use in this connection has been discredited (*Brit. Med. J.*, 2, 425 (1950). (See also Dunlop, *J. Pharm. Pharmacol.*, 1, 1 (1950); D. W. Adamson, *Chem. and Ind.*, Jan. 6, 1951, 2; "Anthisan," "Antistin," "Benadryl," and "Pyribenzamine.")

**ANTI-KNOCK FUELS** — See Motor Spirit.

**ANTIMONY (Sb) and its Compounds** — Atomic weight 121.76. See Elements for other data. Antimony is found naturally in small quantities, but in greater quantities it exists combined with oxygen as so-called *white antimony* ( $\text{Sb}_2\text{O}_3$ ), and in another form as *antimony ochre* ( $\text{Sb}_2\text{O}_4$ ) (sp. gr. about 3.75). Its chief ores are *stibnite* ( $\text{Sb}_2\text{S}_3$ ) or *grey antimony ore*, *antimony blende* ( $\text{Sb}_2\text{O}_3 \cdot 2\text{Sb}_2\text{S}_3$ ) (crystal system 4, and sp. gr. about 4.5), and *red antimony* or *kermisite* ( $2\text{Sb}_2\text{S}_3 \cdot \text{Sb}_2\text{O}_3$ ). Antimony mining is conducted in Asia Minor, Bolivia, Borneo, China, France, Hungary, Mexico, New South Wales, the United States of America, and elsewhere.

Antimony is a bright bluish-white metal largely used in making *type metal*, *stereotype metal*, and *Britannia metal* (all of which give fine and sharp castings), and as an ingredient of some anti-friction or bearing alloys.

The precipitated form known as antimony black is used for producing the appearance of polished steel on papier mâché, pottery, etc.; colloidal antimony in several combinations is used in therapy; the tetroxide is used for rendering enamels opaque, and the trioxide for colouring glass, and as a paint. The red sulphide is used for vulcanizing rubber and for preparing the striking surface on safety-match boxes.

Alloyed with lead, it was largely used in World War I in preparing shrapnel bullets, and the sulphide in making shell primers and as a smoke producer. About 75 per cent. of the antimony used goes into antimonial lead, type metal, linings of brasses, storage battery plates, cable sheaths, lead pipes, lead sheet, and lead foil for collapsible tubes. (See *Strategic Minerals*, by J. B. DeMille (McGraw-Hill Book Co., New York).)

#### ANTIMONY, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country				Antimony Metric tons
Yugoslavia	..	..	2,500	
Czechoslovakia	..	..	900	
Italy	..	..	600	
Germany-Austria	..	..	200	
Portugal	..	..	100	
			<hr/>	4,300
Mexico	..	..	8,100	
U.S.A.	..	..	600	
Canada	..	..	200	
			<hr/>	8,900
Bolivia	..	..	8,200	
Peru	..	..	800	
Argentina	..	..	100	
			<hr/>	9,100
China	..	..	12,000	
Turkey	..	..	500	
			<hr/>	12,500
Algeria	..	..	600	
French Morocco	..	..	200	
Spanish Morocco	..	..	100	
			<hr/>	900
Australia	..	..		500
Sum of above	..	..		36,200

WORLD PRODUCTION, approximately the above.

The metal is prepared by heating the broken-up native trisulphide with half its weight of scrap iron in plumbago and fire-clay crucibles or in a reverberatory furnace, when iron sulphide is formed, and the metallic antimony set free, as follows:  $\text{Sb}_2\text{S}_3 + 3\text{Fe} = 2\text{Sb} + 3\text{FeS}$ ; or the selected sulphide after separation from the associated rocky matter of the ore can be roasted in a reverberatory furnace; the sulphur in this way is burnt off as sulphur dioxide, and the resulting oxide is then reduced by strongly heating with carbon.

When a concentrated solution of the trichloride in hydrochloric acid is subjected to electrolysis, using an anode of ordinary antimony and a cathode of platinum wire, a highly lustrous substance of metallic appearance is deposited on the cathode, and when this is scratched or knocked it becomes strongly heated, due to the increased transformation of a metastable or so-called explosive form of the metal into the more stable form—a change which has been explained by E. Cohen as an instance of monotropy. This explosive difficulty is stated to be overcome by the use of hydrofluoric acid instead of hydrochloric acid. The use of an alkaline electrolyte in place of an acid one presents some advantages: antimony sulphide is dissolved in a solution of sodium sulphide ( $\text{Sb}_2\text{S}_3 + 3\text{Na}_2\text{S} = 2\text{Na}_3\text{SbS}_3$ ), and this can be readily electrolysed.

Increased attention is being paid to various electrolytic methods on account of the high purity of the metal thus produced, and for other reasons.

Antimony is a bad conductor of heat and electricity, and is not acted upon by the air, but when strongly heated it burns in air or oxygen with a brilliant light and forms antimony trioxide ( $\text{Sb}_2\text{O}_3$ ). This oxide, prepared by roasting the sulphide ore in a blast furnace and collecting the vapour, is used as the basis of a white pigment in substitution for white lead. (See "Timonox.")

**Oxides** — The trioxide ( $\text{Sb}_2\text{O}_3$ ) is volatile at relatively low temperatures and occurs in mineral form as *valentinite* and *senarmontite*. It can be prepared by oxidation of the metal and is used as a pigment. The tetroxide ( $\text{Sb}_2\text{O}_4$ ) is practically non-volatile, although it decomposes at  $930^\circ\text{C}$ . into the trioxide and oxygen; it is used in enamel making and known also in mineral form as *cervantite*. It is stated that the pentoxide ( $\text{Sb}_2\text{O}_5$ ) cannot be prepared by direct oxidation, but can be made from potassium antimonate in a wet way. When the trioxide is dissolved in a boiling solution of potassium hydrogen tartrate (*cream of tartar*), potassium antimony tartrate or *tartar emetic* is formed. This compound is used medicinally, and in the leather and dyeing trades.

**Chlorides** — When thrown into chlorine gas the metal takes fire and forms antimony trichloride ( $\text{SbCl}_3$ ); this trichloride is also produced by dissolving antimony sulphide in strong hydrochloric acid and a trace of nitric acid, followed by evaporation to dryness. The trichloride is used in fire-proofing and medicine, and there is a pentachloride ( $\text{SbCl}_5$ ). The trichloride (butter of antimony) is a colourless, crystalline body, soluble in water and alcohol, and is used in bronzing iron, also as a mordant for making lakes and colouring zinc black.

**Sulphides** — Two sulphides are known, both of which are insoluble in water—viz., the trisulphide ( $\text{Sb}_2\text{S}_3$ ), which is used variously as a red pigment, for lining lead chambers used in manufacturing sulphuric acid, and in match making; whilst the pentasulphide ( $\text{Sb}_2\text{S}_5$ ) is used in the manufacture of red rubber, and is known also as “golden sulphide of antimony.” The trisulphide occurs in nature as above stated, and when precipitated from solutions it is an orange-red compound. It is also obtainable from hot solutions in an anhydrous greyish-black form. (See Schlippe's Salt.)

**Hydrides** — Antimony hydride, stibine ( $\text{SbH}_3$ ) is produced when an antimonial solution is brought into contact with zinc and sulphuric acid. It is a colourless gas of offensive odour, which can be obtained also in liquid and solid forms.

**Antimony Sulphate** ( $\text{Sb}_2(\text{SO}_4)_3$ ) — Prepared from the trioxide by action of sulphuric acid, is a white powder decomposed by water and used in pyrotechny.

**Antimony Lactate** ( $\text{Sb}(\text{C}_3\text{H}_5\text{O}_3)_3$ ); soluble in water, and used as a mordant.

**Antimony Fluorides** ( $\text{SbF}_3$  and  $\text{SbF}_5$ )—Soluble in water and used in ceramics.

Antimony forms compounds with the alkyls similar to those of arsenic—for example, **trimethylstibine** ( $\text{Sb}(\text{CH}_3)_3$ ), a disagreeable inflammable liquid. (See Naples Yellow.)

(See “The Chemotherapy of Antimony,” by Gray, Trevan, and Bainbridge (*Chem. and Ind.*, **50**, 215 (1931)); Christiansen, *Organic Derivatives of Antimony*, Amer. Chem. Soc. Monograph (Reinhold Publishing Corp., New York); Morgan, *Organic Compounds of Arsenic and Antimony* (Longmans, Green and Co., London and New York).)

**ANTIMONY VERMILION**—Trade name for antimony trisulphide.

**ANTI-OXIDANT, GASOLINE** (Du Pont) — A solution of normal butyl-para-aminophenol (50 per cent.) in isopropanol (30 per cent.) and methanol (20 per cent.) is No. 5; one of isobutyl-para-aminophenol (50 per cent.) in isopropanol (30 per cent.) and methanol (20 per cent.) is No. 6; and one of disecundary-butyl-para-phenylenediamine alone is No. 22. Used for reducing the formation of gum in gasoline.

**ANTI-OXIDANTS** — Bodies which, when present in small amount, prevent the rapid oxidation of substances otherwise susceptible to that change. Some are used for prohibiting or delaying the rancidity of oils and fats, and articles made from them, such as pastry, the perishing of rubber and linoleum, the formation of gum in petrol, etc. They include many antiseptics, some being of the phenol class and others, such as sodium sulphite, for preventing the oxidation of certain organic compounds. (See Catalysis, Gasoline, Oils, and Rubber.)

**ANTIPYRETICS** — Substances which possess the property of reducing body temperature and are used as febrifuges. Many of them, such as aspirin, phenazone, and phenacetin, also relieve pain.

**ANTIPYRINE** — See Phenazone.

**ANTISEPTICS** — Substances which inhibit or prevent the growth of the micro-organisms causing sepsis or putrefaction. Inhibition may be brought about by direct interference with the living functions of the micro-organisms or indirectly by rendering the medium unfit for their life and multiplication. There are many substances and proprietary preparations of antiseptic character, some of which are described under their respective names. (See "Antiseptics and Disinfectants" in *The Extra Pharmacopœia*, Vol. II, 22nd Ed. (1943); Bacteria, and Disinfectants.)

**"ANTISTIN"** ( $C_{17}H_{19}N_2$ ) — A complex compound, namely, 2-phenylbenzyl-aminomethyl-imidazoline, being one of a series of anti-histamine compounds which are used in medicine for the treatment of allergic conditions such as hay-fever. It is used in the form of its hydrochloride or as a solution of the methanesulphonate for injection.

**ANTITOXINS** — See Bacteria, and Toxins.

**"ANTRYCIDE"** — See Trypanocides.

**"ANTRYPOL"** — A proprietary name for suramin.

**"ANTU"** — Alpha-naphthylthiourea. (See Rodenticides.)

**APATITE** — A mineral compound consisting chiefly of phosphate and fluoride of calcium ( $3Ca_3(PO_4)_2.CaF_2$ ), of crystal system No. 3, and sp. gr. about 3.0; found chiefly in Canada and Norway, although deposits occur in Brazil, the U.S.A., and elsewhere.

#### **A.P.I. (American Petroleum Institute) SCALE OF SPECIFIC GRAVITY**

A modified Baumé scale, used for petroleum.

Degrees A.P.I. = $\frac{141.5}{\text{sp. gr. at } 60^\circ \text{ F.}} - 131.5$ , wherefore			
10°	1.000	40°	0.825
20°	0.947	50°	0.780
30°	0.876	60°	0.738

**APIOL** — A green, oily liquid, obtained from the dried fruit of parsley (*Carum Petroselinum*); sp. gr. 1.055 to 1.091; formerly used in medicine as a diuretic. (See Parsley Oils.)

**APIOLE (Crystalline Apiol)** ( $C_{12}H_{14}O_4$ ) — A white crystalline solid, m.p. 29° to 30° C., slightly soluble in water, freely soluble in alcohol, chloroform, and ether and possessing a persistent parsley odour and a burning taste.

**APOMORPHINE HYDROCHLORIDE** ( $C_{17}H_{17}O_2N.HCl.\frac{1}{2}H_2O$ ) — A colourless substance, being the hydrochloride of an alkaloid obtained by removing the elements of water from morphine when morphine hydrochloride is heated under reduced pressure; slightly soluble in water; sparingly soluble in chloroform and ether. It rapidly becomes green on exposure to air. Apomorphine hydrochloride is used in medicine as an emetic.

**"AQUADAG"** — See Lubricants.

**AQUA FORTIS** — An old name for nitric acid.

**AQUA REGIA** — A mixture of nitric and hydrochloric acids—a very powerful solvent. Gold and platinum, for example, can be dissolved by this mixture, which is commonly made of 1 part and 3 parts of the respective concentrated acids.

**AQUEOUS VAPOUR** (Atmospheric) — See Air, Hygrometer, Hygroscopic, and Water.

**ARABIC GUM** — See Gums and Resins.

**ARABINOSE** ( $C_5H_{10}O_5$ ) — A white crystalline sugar, soluble in water, m.p.  $159^\circ C.$ ; it is a constituent of many plants, and can be made by boiling beetroot chips, gum arabic, or cherry gum with dilute sulphuric acid; chemically an aldopentose. (See Carbohydrates, Glycosides, and Xylose.)

**ARACHIDIC (ARACHIC or EICOSANOIC) ACID** ( $C_{19}H_{39}.COOH$ ) — A member of the normal fatty acids, found in the oil of the earth-nut (*Arachis hypogaea*). It is a crystalline body, m.p.  $75^\circ C.$ , soluble in boiling alcohol and in ether. (See Arachis Oil.)

**ARACHIS OIL (Earth-Nut Oil, Ground-Nut Oil, Nut Oil, Pea-Nut Oil)** — A fatty oil, of which there are many grades, expressed from the fruit (pea-nuts) of *Arachis hypogaea*, a leguminous plant indigenous in India, South Africa, and South America, and cultivated in China, Senegal, Japan, and U.S.A. The oil is pale yellow, of agreeable odour and non-drying character; soluble in alcohol, ether, benzol, and carbon disulphide; has a sp. gr. of 0.916 to 0.925, ref. ind. 1.4612 at  $40^\circ C.$ , sap. v. 185 to 196, and i.v. 85.2. It is used variously as a salad oil and substitute for olive oil, also for soap-making, in the textile trade, in chocolate making, for oiling wood, and as a delicate lubricant for watchmakers' use, etc.

The shelled nuts yield approximately 40–50 per cent. oil, composed mainly of olein, with smaller amounts of the glycerides of linoleic, palmitic, stearic, arachidic, and lignoceric acids. The press cake after expression of the oil is a valuable feed for livestock, being rich in carbohydrates and proteins with considerable fat. The seed coverings are a good source of vitamin. The shells are useful as an insulating material and as a filler in feeds, fertilizers, and plastics.

**ARAGONITE** ( $CaCO_3$ ) — See Calcium.

**ARARA NUT OIL** from the *Joannesia heveoides* Ducke (N.O. Euphorbiaceæ) of Brazil is described as having sp. gr. about 0.924; ref. ind.  $20^\circ C.$ , 1.468; acid v. 0.4 to 2.1; sap. v., 188.5 to 191.6; i.v. (Hubl), about 130; and unsaponifiable content about 0.5 per cent. and useful for soap-making. Both oil and meal have toxic properties.

"**ARASAN**" (Du Pont) — Trade-mark for a seed disinfectant based on tetramethyl thiuramdisulphide. Used as a dust or slurry for the treatment of corn, sorghum, soybean, peanut, and vegetable seeds.

"**ARBONEELD**" (Du Pont) (**Dimethylolurea**) ( $CO(NHCH_2OH)_2$ ) — Trade-mark for urea-formaldehyde thermosetting synthetic resins. Used for moulding compounds, adhesives and finishes, and to impregnate wood to increase its hardness and strength.

**ARBUTIN** — See Glycosides.

**ARCHIL (Orchil)** — A purple dye obtained from many kinds of lichens, including *Roccella tinctoris*, *Roccella Montagnei*, and other species of *Roccella*. It is marketed in three forms, known respectively as archil (paste), persis (dry paste), and cudbear (a reddish powder).

Archil is prepared by tearing the lichen from the trees, drying, grinding to a coarse powder, and then macerating during several weeks in dilute ammonia solution with frequent stirring. The lichens contain certain colourless acids of the type of lecanoric acid which are capable of being transformed into the colourless substance orcin, which is further changed by the action of air and ammonia into the purple substance orcein ( $C_{28}H_{24}O_2N_7$ ). By another method, the lichens are treated with a solution of potassium hydroxide or milk of lime, and the "colouring acids" are precipitated from the extract by hydrochloric or acetic acid.

Archil is used as a dye for cloth, wool, and silk. (See Orcinol.)

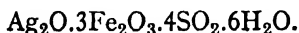
**ARECA (Betel Nuts)** — The dried ripe seeds of *Areca catechu*, cultivated in tropical India, the Philippines and East Indian Islands. It contains a number of alkaloids, the chief of which is arecoline ( $C_8H_{13}O_2N$ ), and is used in veterinary medicine for the treatment of tape-worm. (See Betel.)

**Arecoline Hydrobromide** — A white, crystalline alkaloidal salt; m.p.  $168^\circ$  to  $175^\circ$  C.; soluble in water and alcohol; sparingly soluble in ether, and chloroform.

**ARGEMONE OIL (Mexican Poppy Oil)** — A brownish-yellow oil obtained up to about 36.5 per cent. by extraction from the seeds of the Mexican prickly pear (*Argemone mexicana*, of the natural order Papaveraceæ), unsuitable for paint or edible use, but similar to cotton-seed oil and constituting a useful soap-making material. It is also used as a lubricant and illuminant in Mexico and the West Indies, and the meal left after extraction is a good fertilizer. Its sp. gr. is 0.9220 at  $15^\circ/15^\circ$  C., sap. v. 192.7, i.v. 123.7, acid v. 12, acet. v. 39, and it contains palmitic, stearic, oleic, linoleic, linolenic, and ricinoleic acids, etc.

**ARGENTITE ("Silver Glance")** — A native form of silver sulphide ( $Ag_2S$ ) occurring in cubic crystals (crystal system No. 1), and sp. gr. about 7.2, containing 87 per cent. silver, found in several of the United States of America.

**ARGENTOJAROSITE** — A silver mineral found at Dividend, Utah, having the approximate composition represented by the formula :



**ARGHAN** — A fibre cultivated in the Federated Malay States, said to be superior in tensile strength to all other fibres of its class; of remarkable salt-water resisting quality, and of value in the manufacture of twine, cordages, fishing-net yarns, tapes, and beltings; also possibly qualified to take the place of cotton for all classes of heavy canvas.

**ARGILLACEOUS** — Clay-like in character.

**ARGININE** ( $\alpha$ -Amino- $\delta$ -guanidovaleric acid) — An amino-acid derived from certain proteins by hydrolysis and regarded as a valuable food factor. (See Amino-acids.)

**ARGOL** — Crude tartar as deposited in wine casks or at the bottoms of fermenting vessels. These crystals contain from 60 to 75 per cent. of potassium bitartrate; the higher the alcoholic content of the wine the lower is the amount precipitated, so that ordinary red wines with 9° of alcohol give more than higher grades with 12° to 20° alcohol. The product is used in the dyeing, silver smelting, and baking-powder industries. (See Tartar.)

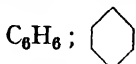
**ARGON** (A) — Atomic weight 39.944. See Elements for other data. Argon is an element found present in the gaseous state in the air to the extent of rather less than 1 per cent. by volume, and also in minute quantity in Bath and other mineral spring waters. It is isolated by processes which remove the oxygen and nitrogen respectively, as, for example, passing a current of air over calcium carbide at 800° C. ( $2\text{CaC}_2 + \text{O}_2 = 2\text{CaO} + 4\text{C}$  and  $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C}$ ). It is a remarkably inert substance, and has been liquefied and frozen to a white solid. It has found application to a large extent for gas-filled electric lamps, the filaments proving less destructible than *in vacuo*, and for an artificial atmosphere in the welding of metals. No chemical combinations of it are known. The density of the gas is 39.94 grams per mole; it is soluble in water to the extent of 4.1 volumes in 100 at 15° C. and boils at -189° C. The fractional distillation of atmospheric argon yields traces of other gases having distinct spectra, and to these Ramsay gave the names of Neon, Xenon, and Krypton. (See Perkin Medal address by W. S. Landis on "An Early Chapter in Argon Production" (*Ind. Eng. Chem.*, **31**, 241 (1939)); and Air.)

"**ARMCO**" — An extremely pure form of iron (99.84 per cent.). Strain hardened "Armco" can be further hardened by temperatures between 150° and 390° C., and both its strain-hardening and temperature-hardening qualities occur during a creep test, while its plasticity is said to decrease and give place to perfect elasticity under conditions of prolonged stress at temperatures below the limiting creep values.

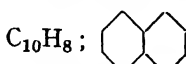
**ARNICA** — The dried flower-heads of *Arnica montana* (Central Europe); used in medicine, as is also the oil obtained from them by distillation. The oil is yellow in colour, has a sp. gr. 0.906, sap. v. 30, and is soluble in alcohol.

"**AROCLORS**" — Chlorinated diphenyl resins.

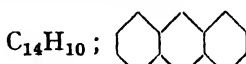
**AROMATIC COMPOUNDS** — Those derived from benzene with one or more benzene rings of carbon atoms as distinct from those of aliphatic or alicyclic character. Examples of aromatic hydrocarbons:



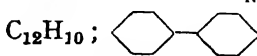
Benzene.



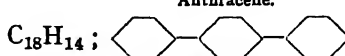
Naphthalene.



Anthracene.



Biphenyl.



1,4-Diphenylbenzene.

**ARRACK** — A spirituous drink containing from 20 to 26 per cent. alcohol, prepared by the fermentation of an infusion of rice. A similar preparation known as "palm wine" is made in Ceylon from coconut toddy.

**ARROWROOT** — See Adhesives, and Starch.

**ARSENIC (As) and its Compounds** — Atomic weight, 74.91. See Elements for other data. Arsenic occurs in nature in Cornwall and elsewhere in the metallic state and in combination with sulphur as *realgar* ( $\text{As}_2\text{S}_2$ ) (crystal system No. 5, and sp. gr. 3.5) and *orpiment* ( $\text{As}_2\text{S}_3$ ). It is also found in other combinations—viz., with iron (*arsenopyrite* or *arsenical iron*,  $\text{FeAs}_2$  and  $\text{Fe}_4\text{As}_3$ ); *mispickel* ( $\text{FeS}_2 + \text{FeAs}_2$ ); with nickel (*kupfernickel*,  $\text{NiAs}$  and  $\text{NiAs}_2$ ), and with cobalt. *Arsenopyrite* occurs abundantly in Ontario, and there are *orpiment* mines in Chitral, while some arsenic is produced in Queensland, Western Australia, Anaconda, U.S.A., France, Sweden, and Cornwall, but it is chiefly produced from the silver-cobalt-nickel-arsenic ores of the Ontario cobalt district as a by-product.

Arsenic is of grey colour, sublimes at  $450^\circ \text{C}$ . without melting, and is used for mixing in small proportion with melted lead to make shots, which are harder than those made with pure lead, and for lead solder.

The metal can be manufactured from arsenical pyrites by roasting it in vessels fitted with suitable condensers for receiving the arsenic which is liberated and volatilized by the splitting up that occurs, ferrous sulphide being left behind:  $\text{FeS}_2, \text{FeAs}_2 = 2\text{FeS} + 2\text{As}$ . In two forms it is crystalline (yellow and metallic), and is a good conductor of heat and electricity, but an amorphous form is also known.

**Arsenic Hydride** ( $\text{AsH}_3$ ), otherwise known as "arsine" and "arsenuretted hydrogen," is an offensive smelling, colourless, poisonous gas which can be prepared by the action of dilute hydrochloric or sulphuric acid upon an alloy of arsenic and zinc. The maximum safe concentration of the gas is 1 part per 100,000 parts of air. It burns with a bluish flame, forming water and arsenious oxide, but if the amount of air is limited, metallic arsenic is deposited. The so-called Marsh's test is based on this change.

**Arsenious Oxide** ( $\text{As}_2\text{O}_3$ ), known also as "white arsenic," occurs naturally as the rare mineral *arsenite*, and is manufactured as a secondary product in the roasting of many arsenical ores for the recovery of the associated metals—copper, nickel, cobalt, silver, and tin—large quantities being recovered from the smelter fume in the U.S.A., chiefly at Butte, Montana, at Garfield, Utah, and at Tacoma, Washington. It is used not only in the manufacture of rat poison, certain pigments, enamels, and opalescent glass, but largely for the preparation of sodium arsenite ( $\text{Na}_2\text{HASO}_3$ ), which is made by dissolving the oxide in caustic soda or sodium carbonate solution, and used as a weed-killer, horticultural insecticide, and wood preservative. The arsenates, however, are said to be less toxic and less destructive to foliage than the arsenites, and although dearer are therefore to be preferred as insecticides. (See Calcium Arsenate, Lead Arsenate, Sodium Arsenates, and Insecticides.) Arsenious oxide is soluble in water and alcohol, and is very poisonous, as are also most of the arsenical compounds.

## ARSENIC

## ARSENIC TRIOXIDE (WHITE ARSENIC), WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country	Arsenic Trioxide Metric Tons
France.. ..	8,000*
Sweden .. ..	8,000*
Belgium-Luxemburg ..	3,000
Germany .. ..	2,200
Italy .. ..	1,000*
	<hr/>
	22,200
U.S.A. .. ..	17,200
Mexico .. ..	8,900
Canada .. ..	800
	<hr/>
	26,900
Brazil .. ..	600
Japan .. ..	3,000*
Australia .. ..	2,500
Sum of above .. ..	55,200
WORLD PRODUCTION ..	59,300

\* Estimated.

Arsenic trioxide was also probably produced in China, Czechoslovakia, Greece, Hungary, Iran, New Zealand, Portugal, Spain, Spanish Morocco, Turkey, United Kingdom, U.S.S.R.

**Ortho-Arsenic Acid** ( $\text{H}_3\text{AsO}_4$ ), prepared by action of nitric acid on metallic arsenic or arsenious oxide, is a white crystalline salt soluble in water, and used as an insecticide.

**Arsenic Pentoxide** ( $\text{As}_2\text{O}_5$ ), a white deliquescent substance soluble in water, is obtained by oxidizing arsenious oxide with nitric acid.

**Arsenic Disulphide** ( $\text{As}_2\text{S}_2$ ) is an orange-red powder insoluble in water, prepared by roasting *mispickel* or other ores containing both arsenic and sulphur, and sublimation. It is used in a number of industries, including calico-printing, the manufacture of leather, shots, and paints, and as a depilatory agent. Its native form (*realgar*), by the action of light, disintegrates to a reddish-yellow mixture of  $\text{As}_2\text{S}_3$  and  $\text{As}_2\text{O}_3$  with some  $\text{As}_4\text{S}_3$ .

The trisulphide ( $\text{As}_2\text{S}_3$ ), which is found native as *orpiment* and is readily precipitated from arsenious solutions by hydrogen sulphide, and the pentasulphide ( $\text{As}_2\text{S}_5$ ) are yellow substances insoluble in water, used as pigments in paint-making.

Arsenic resembles phosphorus and nitrogen in the sense that it forms analogous compounds with alkyl radicals, as, for example, trimethylarsine, which is analogous to trimethylamine and trimethylphosphine.

(See Raiziss and Gavron, *Organic Arsenical Compounds* (Reinhold Publishing Corp., New York); Morgan, *Organic Compounds of Arsenic and Antimony* (Longmans, Green and Co., London); Cacodyl, and Reinsch's Test.)

**ARSENIC ORANGE** — Arsenic disulphide.

**ARSENOBENZENE** ( $C_6H_5.As : As.C_6H_5$ ) is a yellow crystalline body of m.p.  $196^\circ C.$ , derivatives of which have proved of value in the treatment of certain diseases. (See Arsphenamine.)

**ARSINE** — See Arsenic (Hydride).

**ARSPHENAMINE** (“**Salvarsan**”) — A complex organic compound of arsenic, namely, 3,3'-diamino-4,4'-dihydroxyarsenobenzene dihydrochloride, originally introduced by Ehrlich as “Compound 606” for the treatment of syphilis. Arsphenamine is not a chemically pure substance and its use in medicine has been superseded by other less toxic derivatives. The manufacture of arsenobenzene derivatives is controlled by the British Therapeutic Substances Act which prescribes biological tests for therapeutic activity and freedom from undue toxicity.

**Nearsphenamine** (“**Neosalvarsan**,” **Novarsenobenzol**, **Novarsenobenzene**) is the monosodium formaldehydesulphoxylate derivative of arsphenamine. It occurs as a yellow powder; soluble in water, insoluble in alcohol and ether; very readily oxidized and packed in hermetically sealed containers from which the air has been evacuated or replaced by an inert gas. It is the most commonly used organic compound of arsenic in the treatment of syphilis.

“**Stabilarsan**” is the proprietary name of a diglucoside of arsphenamine used as an anti-syphilitic agent.

**Sulpharsphenamine** (“**Kharsulphan**”) is the disodium bisulphite derivative of arsphenamine and occurs as a yellow powder; soluble in water, insoluble in alcohol and ether; very susceptible to oxidation and packed in hermetically sealed containers.

**ARSPHENOXIDE** (**Arsenoxide**) ( $C_6H_6O_2NAs$ ) — An organic derivative of trivalent arsenic, namely, *m*-amino-*p*-hydroxyphenylarsine oxide,

$\begin{array}{c} \text{NH}_2 \\ | \\ \text{O}=\text{As} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \end{array} \text{OH} \end{array}$

It is used as an anti-syphilitic agent and is considered to be superior to nearsphenamine. **Mapharside** (**Mapharsen**) is the hydrochloride of arspenoxide. “**Neo-Halarsine**” is the tartrate of arspenoxide.

“**ARTANE**” (**Trihexyphenidyl**) — A complex organic compound, being the hydrochloride of 3-(N-piperidyl)-1-phenyl-1-cyclohexyl-1-propanol. It is related to atropine in possessing antispasmodic properties and is used in medicine for the treatment of Parkinsonism. (See B. K. Ellenbogen, *Lancet*, 1, 1034 (1950).)

“**ARTIC**” (Du Pont) — Trade-mark for methyl chloride of refrigeration grade. Used for refrigerant and as a fluid for thermostatic and thermometric equipment.

**ARTIFICIAL RADIOACTIVITY** — See Radioactivity.

**ARTIFICIAL SILK** — See Celanese, Cellulose, Rayon, and Silk Substitutes.

**ARUM** — See Starch.

**ARYLS** — A group of radicals, including, *e.g.*, phenyl ( $-\text{C}_6\text{H}_5$ ), originating from aromatic compounds, as distinct from the alkyls, *e.g.*, ethyl ( $-\text{C}_2\text{H}_5$ ). Aniline ( $\text{C}_6\text{H}_5\text{.NH}_2$ ) is typical of the so-called *arylamines*, and ethylamine ( $\text{C}_2\text{H}_5\text{.NH}_2$ ) of the *alkylamines*.

**ASAFÆTIDA** — See Gums and Resins.

**ASARUM OIL** — A volatile oil marketed in two varieties, and used in perfumery. They are distilled from the rhizome and roots of the respective plants, the *Canadense* oil having a sp. gr. of 0.930 to 0.960, and the *European* variety having a sp. gr. of 1.015 to 1.068. These pungent oils contain pinene, linalol, borneol, guaiacol; soluble in alcohol, and ether.

**ASBESTINE (Agalite)** — A mineral occurring in the eastern States of America and South Germany, intermediate in chemical and physical characters between talc and asbestos, of average composition: silica 49.81 per cent., alumina 2.19 per cent., iron oxide 2.8 per cent., magnesia 27.96 per cent., lime 13.21 per cent., and water 3.91 per cent. Freed from its iron content, it is employed as a filler and in the rubber and paint industries.

**ASBESTOS** — A fibrous variety of the mineral *amphibole*, being a compound silicate and aluminate of magnesium, calcium, and iron. The name, however, is applied not only to the minerals *uralite*, *tremolite*, *actinolite*, and other varieties of *amphibole*, but to fibrous forms of *pyroxene*, the different mineral *crocidolite* of the *amphibole* group (distinguished by its large proportion of ferrous iron constituent), and to *chrysotile*, a white fibrous variety of serpentine which differs in that it is the most highly hydrated silicate, whereas some of the others are anhydrous. The three principal varieties are *anthophyllite*, *amphibole*, and *serpentine*.

Large commercial (*chrysotile*) supplies of the serpentine group come from the Province of Quebec, Russia, and Rhodesia, but asbestos occurs also in Cyprus, China, Italy, and the U.S.A. The South African supplies include *chrysotile*, *crocidolite* (blue asbestos), and *amosite*.

Blue asbestos (*hornblende* or *amosite*), found chiefly in South Africa, is reported as superior to the white varieties as a non-conductor, in tensile strength, and resistance to acids, and loses only 5 per cent. on ignition as against 15 per cent. suffered by white asbestos. It is peculiarly suitable for fuming-sulphuric acid plants and as a covering for steam boilers and pipes. Its fibres are longer than those of the ordinary white variety, and it will save 93 to 94 per cent. of the loss from a bare steampipe at over 300 lb. pressure and lasts indefinitely.

The long-fibred asbestos is manufactured into cloth and fabrics for fireproof clothing, theatre curtains, yarn, packing, boiler coverings,

and many other useful commodities, while the shorter fibres are employed for making joints and in compounding a number of building and roofing materials, cements, and paints. It withstands heating to a high temperature, and, as it is not acted upon by many chemicals, is often employed in laboratories; for example, in the form of fibres for plugging the ends of glass tubes in order to retain their chemical contents within prescribed limits; also as a covering or in the form of woven mats or cloths for the central part of wire gauze used on the top of iron tripod stands, thus preventing oxidation by rusting, and affording a softer seat for glass vessels placed thereon when required to be heated

ASBESTOS, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country					Asbestos Metric Tons
Italy	..	..	..	..	7,000
Finland	..	..	..	..	3,000
					10,000
U.S.S.R.	..	..	..	..	100,000*
Canada	..	..	..	..	333,000
U.S.A.	..	..	..	..	11,000
					344,000
Cyprus	..	..	..	..	9,000
Japan	..	..	..	..	1,000*
					10,000
Southern Rhodesia	..	..	..	..	53,000
Union of South Africa	..	..	..	..	23,000
					76,000
Sum of above..					540,000

WORLD PRODUCTION, approximately the above.

\* Estimated

by lamps below, and for the better distribution of the flame. In the fibrous form it is also employed as a filtering material wherewith to plug the neck of funnels for separating solid and liquid materials, particularly when it is known that a paper filter would become easily clogged or destroyed by the particular chemical agent in use; and although the filtrate may not be quite clear, it may then admit of more rapid and perfect filtration through an ordinary paper filter.

The following table of average composition of the principal types is taken from a detailed memorandum prepared by the Natural Resources Intelligence Service, Canadian Department of the Interior, Ottawa. (See Amphibole, Chrysotile, Hornblende, and Uralite.)

	Chrysotile $3\text{MgO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	Crocidolite $\text{NaFe}(\text{SiO}_3)_2 \cdot \text{FeSiO}_3 \cdot \text{H}_2\text{O}(\text{Type})$
$\text{SiO}_2$ .. ..	40.49	51.22
$\text{Al}_2\text{O}_3$ .. ..	1.27	—
$\text{Fe}_2\text{O}_3$ and $\text{FeO}$ ..	2.58	34.02
$\text{MgO}$ .. ..	41.41	2.48
$\text{CaO}$ .. ..	—	0.03
$\text{Na}_2\text{O}$ .. ..	—	7.07
$\text{H}_2\text{O}$ .. ..	14.06	4.50
$\text{MnO}_2$ .. ..	—	0.10

**ASCARIDOLE** ( $\text{C}_{10}\text{H}_{16}\text{O}_2$ ) — A repugnant-smelling organic liquid, namely,  $\Delta^2$ -*p*-menthene-1,4-dioxide, being the anthelmintic principle of chenopodium oil which contains from 60 to 75 per cent. ; b.p. at 15 m.m ,  $108^\circ$  to  $110^\circ$  C. It is used for the treatment of hookworm (ankylostomiasis) (See Chenopodium Oil)

**“ASCARITE”** — A mixture of sodium hydroxide, calcium oxide, and asbestos, used as a carbon dioxide absorbent.

**ASCORBIC ACID** — See Vitamins.

**ASHES** — All vegetable growths, as well as coal, peat, and lignite, leave ashes when burned, and all of them contain some amount of alkali. Potash was originally produced from the ashes of plants. (See Potassium.) Estimated as  $\text{K}_2\text{O}$  it amounts to from about 10 per cent. in the ashes of straw to 42 per cent. in that from peas. The potash is associated with varying amounts of soda, lime, magnesia, iron oxide, sulphur (in the form of sulphates), silica, carbon dioxide, and phosphoric acid. The woods which yield the greatest amount of potash are wormwood and fumitory.

The recovery of fuel from ashes can be at times economically effected by separation due to the difference in the specific gravities of the coke and the clinker, but, of course, the recovered fuel is saturated with water, and until air-dried may contain up to 25 per cent. of water. A more modern treatment in respect of coal is effected by what is known as the Dry Magnetic Process (Ulrich's), which depends upon the presence of iron in the form of pyrites in practically all coals, the separation of the fuel from the clinker being carried out on the periphery of a rotating drum in which two electro-magnets are fixed, the slag being attracted by the field as the ashes pass over the drums, and the non-magnetic coke being automatically projected over a partition and discharged into trucks.

The ash of plant material amounts to approximately 4 per cent., and contains the following elements (in decreasing order of abundance), namely, potassium, sulphur, magnesium, phosphorus, silicon, calcium, sodium, iron, aluminium, chlorine, and manganese.

**ASPARAGINE** ( $\text{COOH}.\text{CH}(\text{NH}_2).\text{CH}_2.\text{CONH}_2$ ) — An acid amide contained in asparagus, potatoes, beetroots, vetches, and the juices of other vegetables including the marsh mallow, liquorice juice, the tubers of the dahlia, and the shoots and young leaves of many leguminous plants. It forms small, hard, inodorous crystals, soluble in 11 parts cold and 5 parts hot water, and when heated with strong acids or alkalis is resolved into aspartic acid and ammonia. It forms certain definite compounds with acids.

**ASPARTIC ACID** (**Asparaginic** or **Aminosuccinic Acid**) ( $\text{COOH}.\text{CH}(\text{NH}_2).\text{CH}_2.\text{COOH}$ ) — A colourless crystalline body of acid taste that is contained in beetroot molasses, and found among the products of the decomposition of many proteins by hydrolysis.

**ASPERGILLUS** — A genus of small fungi or moulds constituting active agents in the decay of various substances and utilized in some industrial processes, four large Japanese industries—viz., rice wine, soy sauce, soy cheese, and *shochu* (a distilled alcoholic liquor) being, for example, dependent upon the use of the fungus *Aspergillus oryze*, which give rise to the enzymes protease and amylase employed in their manufacture. Citric and gluconic acids are among the products of the action of *Aspergillus niger* upon carbohydrates. (See Alcohol, Amylo Process, and Fungi.)

**ASPHALT** — Natural solid or semi-solid bitumen, black or brownish-black deposits of which are found in many places, including Alabama, Trinidad, Alberta (Canada), India, San Valentino, Chieti (Italy), Java, Cuba, Seyssel (on the Rhone), Texas, Utah, Val de Travers (near Neuchatel), Venezuela, Limmer (near Hanover), and St. Jean de Maruéjols (France). They are supposed to have been formed from high-boiling mineral oils by chemical changes including oxidation, melt at from  $32^\circ$  to  $100^\circ$  C., are combustible and largely soluble in carbon disulphide, naphtha, and turpentine. These deposits are known under a great variety of names, including glance-pitch, gilsonite, grahamite, manjak, etc.

Various refined forms of asphalt are used for lining water-tanks, in the construction of asphalt pavings, for binding road materials, for waterproofing, and as components of binding materials, cements, insulating agents, paints and varnishes. Worked up with clay and water in suitable proportions, asphalt is now used for introduction into paper pulp or fibre-board by intercalation, thus increasing the strength and rendering such articles and cartons waterproof and much more durable.

The bituminous constituents of asphalt, which are insoluble in petroleum, closely resemble coal in character, and are termed *asphaltenes*. The content of asphaltenes ranges from 0.25 per cent. in Grosny petroleum free from paraffins to 32.3 per cent. in solid petroleum pitch, the composition being C 85.5 per cent., H 6.8 per cent., O 7.7 per cent., and some sulphur. They are soluble in aromatic hydrocarbons, carbon tetrachloride, and light petroleum. Natural asphalt and petroleum pitch are colloidal solutions of asphaltenes in tars and heavy oils. They

can be separated from tar by dissolving in the minimum amount of benzene or chloroform, and precipitation by addition of light petroleum.

Certain deposits are found in various parts of the world, consisting of aggregates of finely divided mineral matter with liquid oil or semi-solid asphalt, such as the Alberta sands found along the banks of the Athabasca River. The bitumen obtained from these sands yields 18 per cent. gasoline, 13 per cent. kerosene, and 53 per cent. lubricating oils upon distillation. (See Report by Clark and Blair, No. 18 (W. D. MacLean, Edmonton, Canada).) In one method of extraction the sand is warmed to 80° C. with a solution of 1 part per 1,000 of sodium carbonate in water and gently stirred, when segregation rapidly occurs. The aggregates of bitumen ball together, allowing the liquor and sand parts to be drawn off, and the asphaltic material can then be collected and treated as desired. Soap or saponin solutions can be used in place of sodium carbonate. It has been found that the Alberta sand hydrogenated at high temperature and pressure yields at about 280° C. a light oil amounting to 80 per cent. or more of the bitumen, which can be easily refined to produce a satisfactory gasoline. (See *Canadian Journal of Research*, June, 1930.)

The natural rock asphalt, containing varying proportions up to about 20 per cent. bitumen, is converted into so-called "mastic" by melting with a quantity of purer bitumen or a mixture of pitch and mineral oil, so that the product melts at about 76° C. In this form, and in further admixture with sandstone, powdered limestone, or other suitable material, it is used for making pavings and damp courses of buildings.

The Trinidad Lake pitch contains about 40 per cent. asphalt, mixed with clay, mud, and vegetable matter, and after refining it contains about 50 per cent. and 43 per cent. mineral matter with a little water.

The air-blown bitumens are obtained by blowing air through residual oils at a high temperature, whereby condensation products result, varying in consistency from semi-liquid to solid.

Asphaltic bitumens free from tar products present advantages for paving purposes, as phenol, naphthalene, and acridine are dangerous to fish life in the streams into which the drainage from tarred roads may find access.

Bitumen can be prepared in an emulsified form by several methods—viz., by working up a mixture of it with fatty acids or resin, or both, in an alkaline solution, using agitation. Or it can be dissolved in a suitable solvent like benzol and then emulsified with soap and water. Such preparations have been advocated for application to the surface of roads.

"The Chemistry of Bituminous Highway Construction: Native Asphalts" is the subject of a paper by J. S. Miller (see *Chem. and Ind.*, 48, 782 (1929)), who shows in a table the differences in the characters of various asphalt cements (Mexican, Venezuelan, Bermudas, and Trinidad) as employed for paving purposes—that is to say, physical differences which must be related to chemical differences. See also "Determination of Bitumen in Asphaltic Materials," by D. M.

Wilson (*Chem. and Ind.*, **50**, 599 (1931)); D. M. Wilson on "The Bitumen Penetration Test" (*Chem. and Ind.*, **51**, 203 (1932)); *Asphalts and Allied Substances*, by H. Abraham (Crosby Lockwood and Son, London); *The Properties of Asphaltic Bitumen*, by J. P. Pfeiffer, editor (Elsevier Publishing Co., New York and London); Emulsions, Gilsonite, Tar, and Torbanites.

**ASPHALTENES** — See Asphalt.

**ASPHYXIANTS** — Chemical substances which produce suffocation. Fire extinguishers which depend upon the production of gas, such as carbon dioxide, are sometimes termed "asphyxiators." (See Gassing.)

**ASPIRATOR** — An arrangement for aspirating a current of air or other gas by suction through a liquid.

**ASPIRIN** — See Acetylsalicylic acid.

**ASSAYING** — The art of chemically determining the several amounts of metals contained in minerals, ores, alloys, and metallurgical products.

**ASTATINE** (At) — Element 85, prepared artificially, and isotopes extremely unstable, most stable is At 210. Discovered by D. Corson, R. MacKenzie, and E. Segrè in 1940, and name accepted (1949) by the International Union of Chemistry. Astatine is a member of the halogen group, of which chlorine is the familiar element. Astatine 211 is formed by irradiating bismuth 209 with accelerated alpha particles. (See Nuclear Chemistry.)

**ASYMMETRY** — See Isomerism.

"**ATABRINE**" (registered in U.S. Patent Office) ("**ATEBRIN**," favoured by *Chemical Abstracts* and by *British Abstracts*) — See Mepacrine Hydrochloride.

**ATACAMITE** — See Copper.

"**ATERITE**" — A nickel-brass alloy of acid-resisting character of which valves can be made for superheated steam to withstand 250 pounds pressure and 700° C.

**ATM (ATMOSPHERE)** — Unit of atmospheric pressure. (See Barometers.)

**ATMOSPHERE** — See Air.

**ATOMIC BOMB** — See Nuclear Chemistry.

**ATOMIC ENERGY** — See Nuclear Chemistry.

**ATOMIC HEAT** — See Heat (Thermochemical Aspects).

**ATOMIC MASS** — For hydrogen  $1.64 \times 10^{-24}$  gram. For other elements by multiplying this value by the corresponding atomic weight. (See Elements, and Mass-spectrography.)

**ATOMIC NUMBER** — See Frontispiece and Elements for data, and Atoms.

**ATOMIC RADIUS** (See **Elements for data for individual elements.**) — The radius of the imaginary sphere, which is the domain of each atom, so that the distance between any two atoms in a crystalline substance is the sum of the radii of the two atomic spheres (Bragg's Law of Atomic Diameters). These radii are of the order of  $10^{-8}$  cm. Values of the

atomic radius will be found under Elements, and the concept is of considerable value in explaining dipole moments of substances, and the structure of organic compounds.

**ATOMIC VOLUME** — The atomic volume of an element is the atomic weight divided by its density. (See Elements.)

**ATOMIC WEIGHTS** (See *Frontispiece and Elements for data*) of the chemical elements, representing the numbers of the smallest masses that can take part in chemical changes relative to the smallest weight of hydrogen that can similarly function, when oxygen=16.0000 is taken as the standard. "Chemical" atomic weights used in the present work are based on natural oxygen equal to 16.0000 as the standard and were approved by the International Union of Chemistry in 1949. Physicists use as their standard the single isotope-16 of oxygen. (See Atoms, Chemical Interactions, and Elements, where the most recent data are given.)

**ATOMS** — What happens when a piece of matter (*e.g.*, sodium or chlorine) is continually divided into smaller and smaller pieces until they are infinitesimally small? Is matter continuous? Is there a small basic particle which resists further division by ordinary methods or can any tiny piece of matter always be divided again and again, *ad infinitum*?

The Greeks were the first to attempt an answer to these questions. One school of philosophers reasoned that matter was continuous without ever arriving at a final building block. Another school, headed by Democritus about 400 B.C., fathered the shrewd guess that everything was made up of small particles (or atoms) that could not be further divided (discontinuity). This bold idea, which apparently contradicted the sense of sight, remained dormant for almost two thousand years.

The "Cathedral of Atomic Theory" designed by John Dalton in 1808 and "built by the efforts of a few architects and of many workers," was the important milestone in man's understanding of the atom. Dalton's Atomic Theory can be summarized as follows: Every element (see Elements) is made up of minute building blocks called atoms. All atoms of a given element are exactly alike in appearance and weight (see Isotopes). The atom cannot be split into anything smaller (see Nuclear Chemistry). Atoms of different elements differ in weight and properties—thus the difference in the elements. Two or more atoms of different elements may combine to form a group of atoms, called a molecule.

As an illustration consider the elements sodium and chlorine in the light of Dalton's atomic postulates: Subdivide a piece of sodium or some chlorine until it cannot be further divided. This is the atom. Each atom of sodium will be exactly like every other atom of sodium in respect to appearance, size, shape, and weight, and each atom of chlorine is like every other atom of chlorine in these respects. The atom of sodium is different in appearance, size, shape, and weight from a chlorine atom. Finally, an atom of sodium can combine with an atom of chlorine to form a "pair of atoms" called a molecule of sodium chloride. It must be pointed out that the molecule of sodium chloride

is not sodium or chlorine or a mixture of the two, but a new compound substance, NaCl.

As Lord Aston pointed out, it took a hundred years to detect a flaw in the validity of the postulates of the Dalton Theory. This was done when it was proved that atoms of the same element may have more than one fixed weight (isotopes), again when radioactivity was observed, and once more when sub-atomic particles were discovered and utilized in the cyclotronic synthesis of elements and in atomic fission.

A modern understanding of an atom can be obtained by describing it in terms of internal or sub-atomic structure. For this purpose the electron, the neutron, and the proton are recognized as the fundamental building units. (For a more complete discussion of sub-atomic units see Nuclear Chemistry.) The salient features of these units are given in the table :

Unit	Relative Mass	Charge	Location in Atom	Discovered by
Electron ..	0.000549	negative	outside nucleus	J. J. Thomson in 1897
Proton ..	1.007582	positive	in nucleus	E. Rutherford in 1920
Neutron ..	1.008930	neutral	in nucleus	Chadwick in 1932

An atom can be visualized as consisting of a central nucleus of very small dimensions, approximately  $10^{-12}$  cm. in diameter, in which is packed most of the mass and containing a positive charge, surrounded by electrons in organized orbits which give the atom an external diameter of approximately  $10^{-8}$  cm. (The diameter of the atom is approximately  $10^4$  times the diameter of the nucleus.) The mass in the nucleus is due to the presence of protons and neutrons while the positive charge on the nucleus is due to the presence of protons only. The number of electrons in the extra-nuclear orbits is exactly equal to the positive charge, *i.e.*, the number of protons in the nucleus, thus the total atom is neutral. In a chemical reaction the nucleus remains unchanged and only the arrangement of the electrons outside the nucleus is altered.

The atomic weight of an element is practically equal to the sum of the protons and neutrons in the nucleus, the electron weight being negligible by comparison to the total weight. The number of protons in the nucleus of an atom is equal to the number of electrons outside the nucleus, and this number, **Moseley's atomic number**, determines the chemical behaviour of the element. Each element has its own specific atomic number, that is to say, every atom of a given element has the same number of nuclear protons and extra-nuclear electrons. At the same time the number of neutrons in the nuclei of the atoms of a given element may vary, thus making possible more than one atomic weight for an element. For example: The atomic number of sodium is 11 and the atomic weights of its isotopes are 21, 22, 23, 24, and 25 (23 is stable, the others are produced artificially). The atoms

of sodium all contain 11 protons in the nucleus and 11 electrons outside the nucleus, but the number of neutrons in the nucleus varies from 10 to 14 depending upon which atomic isotope is considered. Sodium isotope 21 contains 11 protons plus 10 neutrons in the nucleus and 11 electrons outside the nucleus, while sodium isotope 23 contains 11 protons plus 12 neutrons in the nucleus and 11 electrons outside the nucleus. A similar situation exists for chlorine, atomic number 17, and its isotopes of atomic weights 33, 34, 35, 36, 37, and 38 (35 and 37 are stable, the others are produced artificially).

It is entirely possible for atoms of two neighbouring different elements to have identical atomic weights, called **isobars**, but each element will have its own characteristic atomic number. To illustrate this point, we may select a certain potassium isotope and a certain calcium isotope as follows :

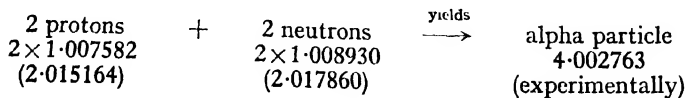
			Potassium isotope	Calcium isotope
Atomic number	..	..	19	20
Atomic weight	..	..	40	40
Number of protons	..	..	19	20
Number of electrons	..	..	19	20
Number of neutrons	..	..	21	20

It should be noted that chemical activity of the elements is directly tied to the atomic number and not to the atomic weight. For example, all the isotopes of the element sodium have the same atomic number and undergo the same chemical reactions. In a like manner all the isotopes of calcium *react* alike, as do the isotopes of chlorine and of potassium.

Atoms of elements which tend to lose control of electrons and become electropositive in a chemical combination display metallic properties, such as sodium does, while atoms of elements which tend to gain control of electrons and become electronegative in chemical combination display non-metallic properties, such as chlorine does.

When the elements are arranged in order of increasing atomic numbers there is a well defined periodicity of recurring chemical properties (Mendeléeff's periodic law).

Whenever mass disappears a corresponding amount of energy is liberated according to the Einstein relationship,  $e=mc^2$ , where  $e$  is the energy in ergs,  $m$  is the mass in grams, and  $c$  is the velocity of light in centimetres per second. The radiant energy of the sun is thought to be due in part to the condensation of light-weight particles into heavier atoms with the loss in mass being liberated as energy. For example, the alpha particle, which is a charged helium nucleus ( $\text{He}^{++}$ ), is known to have a mass of 4.002763 units. It is believed that the alpha particle consists of two protons and two neutrons. The mass equation for the formation of an alpha particle would be :



The sum of the masses of the protons and neutrons obviously gives a value of 4.033024 units and not the experimentally determined value. There is evidently a loss of 0.030261 mass units in the condensation of protons and neutrons to form alpha particles. This loss in mass, called the *packing effect*, is converted into energy whenever sub-atomic particles condense to an atomic nucleus.

The current atomic theory may be regarded as an attempt to characterize the behaviour of atomic particles by varying the distribution of matter and energy according to wave mechanics.

Practical chemistry is still free to deal with the Daltonian atoms as distinct chemical entities. Dampier-Whetham in *A History of Science* in 1939 makes this statement about Dalton: "In his realization that the combining weights of chemical elements give the relative weights of atoms, Dalton made one of the great advances in the history of science, and converted a vague hypothesis into a definite scientific theory." The following statement appeared in the *New York Times* at the time of the meeting of the American Chemical Society in San Francisco in 1935: "For the practical purpose of the laboratory and the factory the atom is still the hard, round, infinitesimal billiard ball that it was when U. S. Grant was president—the ultimate particle. At the San Francisco meeting of the American Chemical Society it was evident that this obsolete atom is still a good working tool." For the non-nuclear chemist this working concept of the atom is still pertinent.

Stewart in his *Recent Advances in Physical and Inorganic Chemistry* (Longmans, Green and Co., London and New York) makes the following quote: "How complex this problem has grown may be guessed by Soddy's ironical comment that the Chemical Society might safely offer a prize of a million pounds to any of its members who could shortly and satisfactorily define the element and the atom for the benefit of and within the understanding of the first-year student of chemistry at the present time."

*References: Atomics for the Millions*, by M. L. Eidinoff and H. Ruchlis (Whittlesey House, McGraw-Hill Book Company, Inc., New York, London); *The Nature of the Chemical Bond*, by L. Pauling (Cornell University Press, Ithaca, N. Y.); *Atoms, Molecules and Quanta*, by A. E. Ruark and H. C. Urey (McGraw-Hill Book Co., New York); *The Particles of Modern Physics*, by J. D. Strathan (Blakiston Co., Philadelphia); *Textbook of Physical Chemistry*, by S. Glasstone (D. Van Nostrand Company, Inc., New York, London); "The Elementary Particles of Physics," by C. D. Anderson (*Amer. Scientist*, **37**, No. 2, April (1949)); "The Eight New Synthetic Elements," by G. T. Seaborg (*Amer. Scientist*, **36**, No. 3, July (1948)); "Man's Attempt to See the Molecule," by H. P. Klug (*Amer. Scientist*, **36**, No. 3, July (1948)); *Phenomena, Atoms and Molecules*, by Irving Langmuir (Philosophical Library, New York); *Sourcebook on Atomic Energy*, by S. Glasstone (D. Van Nostrand Co., New York).

"**ATOPHAN**" — See Cincopen.

**ATROPINE (Daturin)** ( $C_{17}H_{23}O_3N$ ) — A highly poisonous alkaloid obtained by racemisation of *l*-hyoscyamine, extracted from *Atropa*

*Belladonna*, *Hyoscyamus muticus* and other solanaceous plants. It crystallizes in colourless needles or prisms; m.p.  $114^{\circ}$  to  $116^{\circ}$  C.; sparingly soluble in water, soluble in alcohol (1 in 3), and in ether (1 in 16). On hydrolysis with baryta water, it yields tropine,  $C_8H_{15}ON$ , a white crystalline base of m.p.  $62^{\circ}$  C., soluble in water and ether. Atropine is used in medicine, chiefly as the sulphate, to diminish the internal secretions by paralysis of the vagal nerve and for its action in dilating the pupil of the eye; and as an anti-spasmodic agent for the gastro-intestinal tract. (See *Belladonna*.)

**ATTAR OF ROSES (Otto of Roses)** is obtained by distilling the fresh flowers of small white roses known as "Muscata" and of the red variety called *Rosa damascena* with water, and is made in Bulgaria, France, Turkey, Persia, and India, 3 drachms being obtained from 100 pounds of the flower-petals. The Bulgarian rose is the best for the manufacture of this oil, although the other kinds of varying qualities are used. The distilled oil is pale yellow, and contains 70 to 75 per cent. of alcohols including geraniol ( $C_{10}H_{17}.OH$ ) and citronellol ( $C_{10}H_{19}.OH$ ); sp. gr. 0.850 at  $30^{\circ}$  C., ref. ind. 1.460 to 1.465 at  $25^{\circ}$  C., and rotation  $-2^{\circ}$  to  $-4^{\circ}$  at  $25^{\circ}$  C. It also contains an odourless substance (stearoptene) to the extent of from 10 to 16 per cent., consisting of a mixture of two hydrocarbons insoluble in alcohol, and which can be frozen out by cooling the oil below  $16^{\circ}$  C. The odoriferous constituents of the oil are soluble in alcohol. Otto of roses is frequently adulterated with geranium oil, and is chiefly used in perfumery, for flavouring, and preparation of pomades. (Compare Phenylethyl Alcohol.)

**ATTENUATION** — A term used by bacteriologists to signify the weakening of bacterial life, and by brewers to indicate the weakening of worts by fermentation of the contained sugars; also used by chemists concerning the rarefaction or thinning of gaseous bodies.

**A.U. (Ångström Unit)** = 1 ten-millionth of a millimetre) — See Wave-Lengths.

**AUBEPINE (Anisic Aldehyde)** ( $CH_3O.C_6H_4.CHO(1,4)$ ) — A colourless liquid of sp. gr. 1.126 and aromatic odour, made by oxidation of anethole, soluble in alcohol and ether; and used in perfumery, and in the synthesis of the sex hormone stilboestrol.

**AURAMINE** — A dyestuff of the diphenylmethane series.

**AUREOMYCIN** — An antibiotic substance extracted from cultures of *Streptomyces aureofaciens*, a golden coloured micro-organism belonging to the Actinomycetes. It possesses an inhibitory action against the growth of a wide range of organisms including both Gram-negative and Gram-positive species. It has been shown to be more effective than streptomycin against the tubercle organism *in vitro*. It also possesses activity against certain virus infections and has shown promise for the treatment of psittacosis, Rocky Mountain spotted fever, and primary atypical pneumonia. For an account of experimental and clinical trials, see M. S. Bryer, *et al.* in *J. Amer. Med. Ass.*, **38**, 117 (1948).

**AURIFEROUS** — A term applied to ores or minerals containing gold.

**AURINE**  $((\text{HOC}_6\text{H}_4)_2\text{C} : \text{C}_6\text{H}_4\text{O})$  — A dye which crystallizes in beautiful green needles and prisms of a metallic lustre, made by heating phenol with a mixture of sulphuric and oxalic acids to a temperature of from  $130^\circ$  to  $150^\circ \text{C}$ .

**AUSTENITE** — A solid solution of carbon or cementite in the gamma form (or face-centred cubic modification) of iron, and one of the phases in certain steels. Normally austenite is stable at high temperatures, but it can also be stabilized at atmospheric temperatures through such alloying elements as nickel and manganese. These alloys are known as austenitic steels. (See Iron.)

**AUSTRALIAN GUM** — See Gums and Resins.

**AUTOCATALYSIS** — See Catalysis.

**AUTOCLAVE** — A cylindrical vessel having a hemispherical bottom and dished cover, of very stout construction and used for heating liquids under pressure. Heat may be supplied by a steam jacket or by gas burners. When fitted with a stirrer the apparatus is often called a *Digester*. (See *Autoclaves and High Pressure Work*, by H. Goodwin (E. Benn, London).)

**AUTOXIDATION** — Spontaneous oxidation such as the changes which occur when phosphorus or turpentine are exposed to air or oxygen. Some other bodies not otherwise readily susceptible to oxidation become so in the presence of a third substance—*e.g.*, the production of hydrogen dioxide from water and oxygen when zinc is present. (See Catalysis.)

**"AUTROSOL"** — An electrically produced liquid preparation of extremely subdivided carbon and oil, of value in securing engine efficiency in motor-cars. (See "Zollpeer.")

**AUXINS** — See Plant Hormones.

**AUXOCHROMES** — Radicals, such as hydroxyl and amino, which convert a molecule containing a chromophore grouping, such as the azo group, into a dyestuff. (See Chromogens, and Chromophores.)

**"AVANTINE"** — See Isopropyl Alcohol.

**"AVERTIN"** — See Bromethol.

**AVIATION VARNISHES** — See Dopes.

**AVOCADO FAT** — An edible oil prepared from the fruit of the *avocado* or *aguacate* (Brazilian) pear, and used in America for soap-making.

**AVOGADRO'S LAW** — See Molecules.

**AZEOTROPIC DISTILLATION** — See Distillation.

**AZIDES** — Compounds containing the group— $\text{CO.N}_3$  are known as acid azides, and others, such as sodium azide ( $\text{NaN}_3$ ), regarded as salts of hydrazoic acid (azoimides), containing the group— $\text{NN}_2$  or  $-\text{N}_3$ . Some of these are used in preference to fulminating mercury as detonators and priming agents, because they require a higher temperature, as a rule, to bring about detonation, and are therefore safer.

Silver azide ( $\text{AgN}_3$ ) is a white substance insoluble in water, and can be obtained in fine crystals by dissolving silver nitrate (40 grams) in water (50 c.c.) and adding the solution to a solution of sodium azide (13.5 grams) in water (70 c.c.).

H. Kast and A. Haid have given the following temperatures of ignition: cyanuric triazide  $205^\circ$ , lead azide  $355^\circ$  to  $360^\circ$ , mercury fulminate  $215^\circ$ , mercury fulminate chlorate mixture  $215^\circ$ , and lead styphnate  $270^\circ \text{C}$ . (See Hydrazoic Acid (Hydrogen Azide), and Lead (Azide).)

**AZINES** — Heterocyclic compounds of six atoms in the ring, one or more of which atoms is nitrogen, thus pyridine  $\left( \begin{array}{c} \text{CHCHCHCHCH} \\ | \text{---} \text{N} \text{---} | \end{array} \right)$ ; pyridazine  $\left( \begin{array}{c} \text{CHCHCHCH} \\ | \text{---} \text{N} \text{---} \text{N} \text{---} | \end{array} \right)$ ; and of resonance constitution resembling benzene.

**AZO COMPOUNDS** — These contain the group  $\text{—N:N—}$ , but the members are not all dyestuffs. (See Dyes.)

**AZO DYES** — See Dyes and Dyeing.

**AZOLES** — Heterocyclic compounds of five atoms in the ring, one or more of which atoms is nitrogen, thus pyrrole  $\left( \begin{array}{c} \text{CH : CH.CH : CH} \\ | \text{---} \text{NH} \text{---} | \end{array} \right)$ ; pyrazole  $\left( \begin{array}{c} \text{CH : CH.CH} \\ | \text{---} \text{NH.N} \end{array} \right)$ .

**AZURITE (Chessylite)** — See Copper.

**AZOXYBENZENE**  $\left( \begin{array}{c} \text{C}_6\text{H}_5\text{N} : \text{N} \text{C}_6\text{H}_5 \\ \text{O} \end{array} \right)$  — A yellow solid, of m.p.  $36^\circ \text{C}$ . and usually made by refluxing nitrobenzene with alcoholic sodium hydroxide, and crystallizing from hot alcohol solution.

**BABASSU OIL (Babaçu Oil)** — Obtained from *Orbignia martiana*, a palm tree grown in Brazil; has an oil content of 67 per cent., i.v. of 15.6, sap. v. 247.7, m.p.  $26^\circ \text{C}$ . The oil is valuable for margarine and other edible uses such as in confectionery.

**BABBITT METAL** — An alloy of tin, antimony, and copper, used for bearings, etc. The metal is made of varying proportions of the constituents according to the intended application. One description is given as consisting of 89 parts tin, 7.5 antimony, and 3.5 copper, whilst that of "hard" character is said to be an alloy of 83.3 tin, 8.3 antimony, and 8.3 copper. Another of the composition: tin 83 per cent., antimony 10.5 per cent., copper 2.5 per cent., and lead 4 per cent., resists the effects of impact well.

**BACILLOSPORIN ("Aerosporin")** — An antibiotic substance isolated from cultures of the soil organism, *B. aerosporus*. Chemically, it is a basic peptide and the hydrochloride has been prepared in the pure

state. One milligram of the pure hydrochloride contains 10,000 units of activity. It is bactericidal against Gram-negative organisms and *in vivo* tests have shown that it is effective against experimental infections due to *Hæmophilus pertussis* (the organism responsible for whooping cough), *Eberthella typhosa*, and *Escherichia Coli*. It has a more restricted action than streptomycin. (See G. C. Ainsworth, A. M. Brown and G. Brownlee, *Nature*, London, **160**, 263 (1947). For a report of its use in the treatment of pertussis, see P. N. Swift, *Lancet*, **1**, 133 (1948).)

**BACITRACIN** — An antibiotic substance isolated from the culture fluid in which *Bacillus subtilis* has been grown. It is active against *Streptococcus pyogenes* and *Treponema pallidum*. Bacitracin is a polypeptide consisting of phenylalanine 11 per cent., leucine 9 per cent., isoleucine 22 per cent., glutamic acid 10 per cent., aspartic acid 17 per cent., lysine 9 per cent., histidine 10 per cent., cystine 14 per cent., and ammonia 1.5 per cent. (see Barry, Gregory and Craig, *J. Biol. Chem.*, **175**, 485 (1948)). The production and properties of crude bacitracin are described by Anker, Johnson, Goldberg and Meleney, *J. Bact.*, **55**, 249 (1948). For an account of the stability of bacitracin in pharmaceutical preparations, see Bond, Himelick and Macdonald, *J. Amer. Pharm. Ass. (Sci. Ed.)*, **38**, 30 (1948).

**BACTERIA (Micro-organisms, Microbes)** were first observed under the microscope by Leeuwenhoek (1632–1723), but the science of bacteriology can only be considered to date from the time of Pasteur (1822–95). Bacteria are minute unicellular vegetable organisms, usually only a few thousandths of a millimetre in length. They are commonly grouped in the following categories: **Bacilli**, comprising rod types which, under certain conditions, form endospores, which constitute a resting stage and are more resistant to an adverse environment than the vegetative cells; **Bacteria**, comprising rod types which do not form endospores; **Cocci**, types which are in general spherical and comprise, according to the method of subdivision of the cells, such forms as *Streptococci*, in which the cells occur in chains, *Staphylococci*, in which the cells are in clumps, and *Sarcinæ*, in which the cells divide in such a manner as to form cubical packets of eight or more cells; **Spirilla**, in which the cells are in the form of a spiral of several turns, that is, are “corkscrew-shaped”—in some cases the organisms exhibit only a section of a turn, that is, are “comma-shaped,” when they are designated *Vibrios*.

Many species of bacteria and bacilli, and all spirilla, possess one or more exceedingly fine thread-like appendages termed flagella, which protrude from the surface of the cell and are only visible by dark ground illumination or special staining. The lashing movement of the flagella imparts motility to the organism.

Whereas most bacteria are devoid of colouring matter, certain types produce distinctive pigments when grown on particular substrates: e.g. *Bact. prodigiosum* (*Serratia marcescens*) has a vivid red colour, *Bact. violaceum* violet, *Bact. pyocyaneum* a fluorescent blue, and a

number of types, such as *Micrococcus luteus*, *Bact. sulphureum* and *Staphylococcus pyogenes aureus* produce various yellow pigments.

Many systems of classification of bacteria have been suggested. Those at present employed are based on both morphological and physiological characters, the former affording a basis for the broader divisions, and the latter, more generally, for specific differences. It is doubtful whether a classification based on purely serological reactions could be practical for all types, and it seems advisable, in the present state of knowledge, to retain the existing systems, in which a certain broadness of definition is an advantage rather than a handicap.

Reproduction in the bacteria appears to be entirely by simple fission: a cell elongates, forms a transverse septum, and divides into two exactly similar daughter cells, which theoretically may repeat the process indefinitely. In the simplest cases the whole life cycle may be completed in about twenty minutes, so that in a few hours a single bacterium can give rise to many millions of cells. The optimum rate of growth is not, however, maintained for long, on account of the retarding factors which come into play, such as depletion of food material and accumulation of toxic products of the organism's own metabolism.

While the origins of modern bacteriology are to be found in Pasteur's earlier work in the non-medical field, from the time he turned his attention to certain pressing problems of human diseases, bacteriology outside the medical sphere showed very restricted development until the last few decades. There is now to be found a general appreciation of the wide field covered by microbiology, of which medical bacteriology is only one, though a very important, aspect, and which is outside the purview of this work. Much greater attention than hitherto is now being devoted to industrial and economic bacteriology, and as the inevitable concomitant of the present social system there have grown up such important subdivisions as the bacteriology of Water, Milk, Sewage, and Canning.

Bacteria play a most important part in the life of nearly all animals and plants. Many diseases are caused by bacteria, including anthrax, diarrhoea, dysentery, gangrene, pneumonia, tuberculosis, yellow fever and many others. Bacteria also perform many functions beneficial to animal life. The assimilation of food substances in the intestinal tracts of many animals is assisted by the bacterial flora of the digestive system. Certain feedstuffs and foods, such as ensilage, cheese, sauerkraut, and bread are prepared with the aid of micro-organisms.

No less than animals, plants depend on bacteria for the production of nutrient substances. The organic matter of soils is decomposed largely through the agency of soil bacteria. Certain bacteria, notably the *Azotobacter* species, possess the ability to fix atmospheric nitrogen, and in this way add tremendously to the supply of this important element available to plants.

The industrial use of bacteria has developed in many ways in recent years. Yeasts, which are related to bacteria, have been employed for many years in the production of fermented wines, beers, and other liquors. By the selection of proper bacterial species it is possible to produce pure

produce organic acids, acetone, glycerol, and other alcohols. The commercial preparation of coffee, cocoa, tobacco, and flax is accomplished with the aid of bacteria. It has been suggested that the formation of petroleum and coal was aided by bacterial action.

(See *Physiology and Biochemistry of Bacteria*, R. E. Buchanan and E. I. Fulmer (Baillière, Tindall and Cox, London); *A System of Bacteriology in Relation to Medicine*, various authors, under the auspices of the Medical Research Council (H.M. Stationery Office, London); *Bacterial Metabolism* (2nd edition), M. Stephenson (Longmans, Green and Co., London); *Chemical Activities of Micro-organisms*, A. J. Kluyver (University of London Press); *Principles of Solid Microbiology*, S. A. Waksman (Baillière, Tindall and Cox, London); *Microbiology of Cellulose, Hemicelluloses, Pectin, and Gums*, A. C. Thaysen and H. J. Bunker (Oxford University Press); *Microbiology of Starch and Sugars*, A. C. Thaysen and L. D. Galloway (Oxford University Press); *Review of the Physiology and Biochemistry of the Sulphur Bacteria*, H. J. Bunker (H. M. Stationery Office, London); *Cattle Fodder and Human Nutrition*, A. I. Virtanen (Cambridge University Press); *Survey of the Biochemical Activities of the Acetic Acid Bacteria*, K. R. Butlin (H.M. Stationery Office, London).)

**BACTERICIDE** — A substance which possesses the property of killing micro-organisms. Many substances, of varying chemical type, exert a bactericidal action, the main classes being phenols, chlorinated phenols, aniline and acridine dyes, oxidizing agents, and mercury compounds. (See "Antiseptics and Disinfectants," *The Extra Pharmacopœia*, Vol. II, 22nd Ed. (1943); Antiseptics, Bacteria, and Disinfectants.)

**BACTERIOSTATIC** — A substance which inhibits the growth of bacteria. (See Antiseptics.)

**BACURY KERNELS** — Seeds of *Platonia insignis*, of the natural order of Guttiferæ, from South America; they yield about 70 per cent. of a fat of m.p. 34.4° C., sap. v. 191.8 and i.v. 63.3.

**ADDELEYITE (Brazilite)** — See Zirconium.

**BAGASSE (Bégasse)** — See Sugar.

**"BAKELITE"** — Trade-name for phenol, polyethylene, polystyrene, urea, and other synthetic resins and plastics. The phenol type is made by condensing equimolecular quantities of phenol and formaldehyde in the presence of a small quantity of a base, and the reaction occurs in two stages: (1) condensation of the two substances in the presence of a catalyst, resulting in the formation of a liquid or viscous product, soluble in alkali, glycerine, acetone, etc.; and (2) transformation of the first product into an insoluble and infusible mass by heating it at a temperature of about 300° to 350° F. under pressure of about 1,500 lb. per sq. inch of mould surface. Among other applications used as a binder for the material of grinding-wheels. In admixture with quartz it has been used for lining pipes in which warm chlorine gas circulate, and as a homogeneous combination with selected

asbestos fibres it has found employment as an acid-resisting constructional material in respect of hot or cold hydrochloric acid and many metallic salts. (See Gums and Resins (Synthetic).)

**BAKING POWDERS**—Baking powders are preparations used as substitutes for yeast in making bread of a spongy character, by the production of carbon dioxide in the dough. The joint use of tartaric acid and sodium bicarbonate will produce such a result, for example. Besides tartaric acid, as acidic materials, there are in use potassium acid tartrate (Cream of Tartar), sodium acid pyrophosphate, mono-calcium phosphate ( $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ), and sodium aluminium sulphate. Corn starch of low-moisture content is required to be added to maintain stability during storage. Modified baking powders may contain calcium lactate, or dried cultured buttermilk of high acidity, the use of which is covered by patents. The Inland Revenue department of the Canadian government has conducted periodical surveys of the quality of baking powders offered for sale. The department considers that 12 to 13 per cent. of evolved carbon dioxide is a normal value for this product. The minimum value according to United States Definition and Standard is 12 per cent. available carbon dioxide. A baking powder which does not leave any mineral residue uses acctonedicarboxylic acid which decomposes into carbon dioxide, water, and acetone. (See Calcium (Biphosphate), Fermentations, Potassium (Bitartrate), Wheat, and Yeast.)

**BAKOBY OIL**—See Tung Oil.

**B.A.L. (British Anti-Lewisite)**—See Dimercaptol.

**BALANCES**—Instruments for the determination of weights made of great variety and some of extreme delicacy. The ordinary form is constructed upon lever principles, and consists of a beam supported at the middle of its length, and suitably connected with weighing-pans suspended from the extremities of the lever beam, with agate knife edges working on agate planes and rider slides traversing the beam.

The assay balance used by the Royal Mint, Royal Arsenal, and Assay Offices is designed to carry 2 grams on each pan and to turn with 0.01 milligram. Another one with "Chainomatic" attachment secures a sensitivity of 0.0001 gram without weights or riders below 0.1 gram, a length of fine chain attached to the balance beam taking the weights below that figure.

There are so-called micro-balances of very sensitive character of which the capacity is 20 grams, and the sensitivity at full load is 0.001 milligram.

The micro-balance used by Ramsay and Gray depends for its sensitivity upon the change in buoyancy of a small quartz bulb suspended in air when the pressure is varied.

The "Aperiodic" balance has an air-damping device for reducing the swing period and is provided with a micro-scale and microscope for accurate reading.

The "Precision Torsion" balance is specially constructed for the accurate weighing of threads to compute the "denier" and for use in the electric lamp industry and Bang's blood-sugar test.

**BALATA** — The rubber gum, or coagulated latex of *Mimosa globosa*, a forest tree of the order Sapotaceæ, which grows in British and Dutch Guiana, Venezuela, and elsewhere, known otherwise as the "bully tree." It largely resembles gutta-percha in nature and properties but contains more resin, and finds many similar commercial applications. Its stress-strain characteristic is inferior to that of rubber and it vulcanizes more slowly.

**BALLING SCALE** — See Hydrometers.

**BALSA** — The wood of a South American tree, *Ochroma Lagopus*, found chiefly in Ecuador. It is less dense than cork and can be worked with ordinary wood-working tools. Balsa wood is used in life-jackets, for model making, and as a heat-insulating material.

**BALSAMS (Oleoresins)** are natural products consisting of essential or volatile oils admixed with resins, which, in some cases, are supposed to be derived from the oils by chemical changes, including atmospheric oxidation; used in perfumery, varnish making, medicine, etc.

**Canada Balsam** or **Canadian Turpentine** is produced by *Abies balsamea*, a conifer which grows in Canada, Virginia, Carolina, etc., and, like all the turpentines, is produced by making incisions in the bark. In common with other crude turpentines, when distilled it yields turpentine oil and leaves resin behind in the retorts. It is a yellowish viscid liquid, of pleasant odour and bitter taste, soluble in ether, chloroform, and benzol.

**Copaiba Balsam (Balsam Capiwi)**, produced by several varieties of *Coparifera* indigenous in Brazil, Peru, Mexico, and the Antilles, flows from incisions made for that purpose in the trees during rainy weather, and in this form it is a syrupy, oily liquid varying in character and properties according to the species of trees from which it is obtained. By exposure to the air it becomes solid, and is used in medicine, also in preparing lac varnishes and tracing paper. It is soluble in alcohol, ether, chloroform, benzol, and carbon disulphide; sp. gr. 0.940 to 0.990.

**Dragon's Blood** — A red resinous secretion on the fruits of *Dæmonorops propinquus*, *D. Draco*, and other species of *Dæmonorops*, a number of palms indigenous to Sumatra and the West Indies. It contains benzoic and benzoylacetic acids in combination with drachoresinotannol and is used variously in the process-engraving and lithographic trades, for colouring mahogany varnishes, and in preparing gold lacquers.

**Friar's Balsam** — An alcoholic solution of aloes, benzoin, styrax, and tolu balsam.

**Mecca Balsam** or **Balm of Gilead** is the product of the *Balsamodendron gileadense*, a terebinthaceous shrub, native of Arabia Felix. There are several varieties, and the finest quality of fragrant odour is said to exude from the flowers, whilst an inferior quality is obtained from incisions in the branches. It is not much used in medicine now, but in the East it is used as a tonic.

**Barium Chloride** ( $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ ), a colourless crystalline salt, is obtained by dissolving the native carbonate in hydrochloric acid, just short of neutralization, so that any iron present remains in the precipitated state, and from the solution, the salt, which is very soluble in water, is crystallized out in rhombic tablets. It is also made by reduction of barium sulphate to sulphide with carbon, and decomposition of the resulting sulphide with hydrochloric acid. In another process, briquettes of barium sulphate, lime, and magnesium chloride, together with lignite, are heated in a reducing furnace for some hours; calcium chloride is first formed, and this reacts with the barium sulphate, forming calcium sulphate and barium chloride, which can then be washed out. It is used in the leather industry, as a rat poison, in making boiler compounds, and as the most common soluble barium salt.

**Barium Sulphate (Barytes)** ( $\text{BaSO}_4$ ) — When barium chloride in solution is mixed with a dilute solution of sulphuric acid, insoluble barium sulphate is precipitated. It occurs in the forms of finely ground *heavy spar*, of crystal system No. 4, and sp. gr. 4.3 to 4.7. Both forms are used in the paper, textile, and rubber industries as a filler, also in compounding lithopone, other distinct pigments (including *permanent white* and *blanc fixe*), and for admixture with white lead in paint-making. *Blanc fixe* used as a base for lake colours does not serve well unless admixed with a proportion of aluminium hydroxide. (See Paints.)

**Barium Nitrate** ( $\text{Ba}(\text{NO}_3)_2$ ) is obtained by dissolving *witherrite* in dilute nitric acid. It crystallizes in large colourless octahedra; is soluble in water, but not so soluble as the chloride, and is used in pyrotechnics for producing green colouration.

**Barium Sulphide** ( $\text{BaS}$ ) is a yellowish-green substance, soluble in water, sometimes used as a luminous paint, as it possesses, in common with calcium sulphide the property of emitting a feeble phosphorescent light in the dark. It is also used as a depilatory, in vulcanizing, and for weighting gutta-percha. It is commercially prepared from barium sulphate by reduction with coal powder in suitable ovens, and subsequent leaching of the reduced mass with water, which yields a solution really consisting of barium hydrosulphide and some hydroxide. The product yielded upon evaporation is used in making lithopone.

**Barium Oxides** — There are two oxides of barium, white insoluble bodies, namely, the monoxide ( $\text{BaO}$ ) and dioxide ( $\text{BaO}_2$ ), the last named of which is used as a bleaching agent and in the manufacture of hydrogen dioxide. When the monoxide is slaked with water it gives rise to the formation of the hydroxide ( $\text{Ba}(\text{OH})_2$ ), which is soluble in hot water, can be obtained in crystalline form, and is used in the sugar industry and in oil refining.

**Barium Acetate** ( $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ ) — A white crystalline salt, soluble in water, used as a chemical reagent.

**Barium Aluminate** ( $\text{Ba}(\text{AlO}_2)_2$ ) — Made by roasting a mixture of barytes, bauxite, and coke, followed by extraction with water; is useful as a water-softener for boiler supplies.

**Barium Carbonate** ( $\text{BaCO}_3$ ) — A white compound insoluble in water,

prepared from barium sulphide by action of sodium carbonate. In the form of a paste (with or without liquid extract of squills), it is regarded as one of the most effective poisons for rats. A mixture, largely used in India, is prepared from :

Barium carbonate	..	..	..	..	6 ounces.
Common salt	..	..	..	..	$\frac{1}{2}$ ounce.
Wheat flour	..	..	..	..	4 ounces.
Pea or bajri flour	..	..	..	..	12 „
Dripping or ghee	..	..	..	..	4 „

This quantity is sufficient for 1,000 baits. The dripping or ghee is melted, and the whole mixture worked into a paste or dough, rolled out, and cut up into small squares. Barium carbonate is also used in the china and porcelain manufactures. The mineral is *witherite*.

**Barium Caseinate** is a good wetter. (See Wetting Agents.)

**Barium Chlorate** ( $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ ) — White, crystalline, soluble in water, and used in pyrotechnics for green colouration and dyeing.

**Barium Chromate** ( $\text{BaCrO}_4$ ) — A heavy, yellow, crystalline body, insoluble in water, used to a small extent in compounding pigments and making safety matches.

**Barium Cyanide** ( $\text{Ba}(\text{CN})_2$ ) — White, crystalline, soluble in water and alcohol ; used in metallurgy.

**Barium Fluoride** ( $\text{BaF}_2$ ) — A white powder, slightly soluble in water, used in enamel-making.

**Barium Bromide** ( $\text{BaBr}_2 \cdot 2\text{H}_2\text{O}$ ) — A crystalline salt soluble in water, used in making other bromides.

**Barium Manganate** ( $\text{BaMnO}_4$ ) — Insoluble in water, and used as a pigment.

**Barium Thiocyanate (Sulphocyanide)** ( $\text{Ba}(\text{CNS})_2 \cdot 2\text{H}_2\text{O}$ ) — A white, crystalline, poisonous body, soluble in water, used in making some other thiocyanates.

All the soluble salts of barium are poisonous, and colour a Bunsen flame green when pure.

**BARLEY** — See Malt.

**BARM** — Mixture of wort and yeast ; the name is given also to the yeasty top which forms on fermenting beer, used as leaven in bread-making and for other fermentations. (See Beer, and Yeasts.)

**BAROMETER** — An instrument devised for indicating the pressure or density of the air. They are made in various forms, of which the simplest consists of a straight glass tube closed at one end, filled with mercury, and inverted with the open end in a tray of mercury. The standard density of air is when, at sea-level and at a temperature of zero ( $0^\circ \text{C.}$ ), the column of mercury in the tube stands at 760 millimetres, or 29.92 inches high. As the pressure or density of the atmosphere increases the column rises, and as it diminishes the column falls. This normal pressure corresponds to about 14.7 pounds to the square inch, or 1,012,630 dynes per square centimetre.

The space above the mercury, in the simplest form of a mercurial barometer, is popularly known as the Torricellian vacuum.

As the barometer measures the weight of the superincumbent air, it necessarily follows that the higher the altitude the lower the barometer indication. In chemical investigations, gases are weighed or measured subject to the atmospheric pressure, and as their volumes vary directly with the temperature and inversely with the pressure, the necessity arises of recording the pressure and reducing the amount to a standard pressure and a standard temperature respectively.

Aneroid barometers are constructed without the use of liquids, and are dependent upon the effect of atmospheric pressure on the elastic sides of an exhausted metal box. The barograph is constructed on this principle, and is provided with clockwork and a driven pen, which records the variations of pressure upon a chart.

**BAROSCOPE** — A U-tube containing liquid and connected so that pressure difference in the two arms can be observed.

**BARRILLA** — Impure sodium carbonate, somewhat like kelp, produced in Spain and the Levant by burning certain plants (genus *Salsola*), which grow on the seashore, to ashes.

**BARWOOD (Camwood)** — An African red dye-wood from the *Baphita nitida*, which contains 23 per cent. of red colouring matter soluble in hot alcohol, supposed to be identical with "santalin" (a crystalline red body obtained from sandal wood). (See Sandal Wood.)

**BARYTES (Heavy Spar)** — See Barium (Sulphate).

**BARYTOCALCITE** — A mineral compound carbonate of barium and calcium of the composition  $\text{BaCO}_3, \text{CaCO}_3$ .

**BASALT** — A dark-coloured fusible form of felspar of volcanic origin, harder than granite, from which apparatus of high acid-resisting quality may be manufactured. It contains about 50 to 60 per cent. silica, 10 to 15 per cent. alumina, and small proportions of iron oxide, lime, soda, potash, and magnesia. It can be melted and cast at about  $1,400^\circ$  to  $1,500^\circ \text{C.}$ , and is not disintegrated by the electric current, thus admitting of its use for making high-tension insulators.

**BASE EXCHANGE** — See Ion Exchange.

**BASES (Alkalis)** — See Acids and Bases.

**BASICITY** — The number of hydrogen atoms contained in an acid which can be replaced by a base or metal. (See Acids.)

**BASIC SLAG** — See Concrete, and Iron.

**BASSORA GUM** — See Gums and Resins.

**BASSWOOD (LINDEN) OIL** — From *Tilia americana*; it is like cotton-seed oil, and contains glycerides rich in butyric acid.

**BATEING** — See Tanning.

**BATTERIES (Electrical)** — See Electricity (Electrochemical Aspects).

**BATTERIES (Storage)** — See Electricity (Electrochemical Aspects).

**“BATTERIUM” METAL** — An anti-corrosive copper-aluminium-nickel alloy of density 7.67, m.p. 1,050° C., tensile strength 35 to 45 tons per sq. in., Brinell hardness 158 to 168. Useful for apparatus used with organic acids, alkalis, super-heated steam, bleaching, and dye-stuff liquor.

**BAUMÉ SCALE** — See Hydrometers.

**BAUXITE** — See Aluminium.

**BAYBERRY (Candleberry)** — See Waxes.

**BAYER 205** — See Suramin.

**BAY OIL (Myrcia or Bayberry Oil)** — A yellowish essential oil distilled from the leaves of the West Indian *Pimenta acris* (*Myrcia acris*), which contains from 2 to 3 per cent. of the oil; sp. gr. 0.945 to 0.990 at 15° C., ref. ind. 1.500 to 1.520 at 20° C. Yield from 2 to 3 per cent.: used in perfumery and for making bay-rum. It contains pinene, chavicol (a phenol  $C_9H_{10}O$ ), citral, and eugenol.

The essential oil of *Laurus nobilis*, produced in Northern Italy from the leaves and containing cineol, is not identical with the myrcia oil.

**BAY SALT** is produced by the evaporation of sea-water.

**“BEATL”** — Proprietary name of a formaldehyde-thiourea condensation product, a synthetic resin.

**BECQUEREL RAYS** — See Radioactivity.

**BEECHNUT OIL** (from *Fagus*, a genus of Cupuliferæ, including a number of species) is stated to contain as follows:

<i>a</i> -Linolenic acid	.. ..	0.39 per cent.
<i>a</i> -Linoleic acid	.. ..	9.19 ..
Oleic acid	.. ..	76.69 ..
Palmitic acid	.. ..	4.88 ..
Stearic acid	.. ..	3.45 ..
Phytosterol, etc.	.. ..	0.82 ..

It is stated to be equal in flavour with olive oil and to keep well, finding domestic use, while the marc is a good cattle food.

**BEER** — Infusion of malt, flavoured with the bitter of hops and fermented with yeast, containing from 2 to 6 per cent. of alcohol. Porter and stout owe their dark colour and special flavour to the employment of added colouring matters or “high dried” malt, but roasted or semi-roasted malts must be used to reach the intense coloration that is desired. Caramel is added mainly for flavouring. Any farinaceous grain can be used, but barley is generally preferred. It is allowed to germinate, and subsequently kiln-dried, converting it thereby into malt, and the higher the temperature at which it is dried the darker becomes the colour. By the process of germination, diastase is formed from the albuminoid part of the grain, and (as explained later) the starch is converted by the diastase into dextrin, malto-dextrin, and maltose, which in their turn are converted into alcohol by the subsequent fermentation with yeast. This, however, is not allowed to proceed to completion, so that some sugar may be left in solution after the yeast is separated from the fermented wort.

While by the action of enzymes a certain amount of ready-formed soluble carbohydrates is formed during the malting process, it is in the mash tun that diastase exercises its fuller function of saccharifying (hydrolysing) the starch of the malt. This starch is sometimes supplemented by the addition of other starchy substances, such as maize, rice, or barley, which have been previously gelatinized by heating with or without a little malt—starch is changed into dextrin, and, according to the active capacity of the enzyme, the measure of modification of the malt, and the temperature employed, into malto-dextrin and maltose. By the action of the enzyme maltase the sugar maltose is changed into dextrose prior to this being itself changed by the enzyme zymase into alcohol and carbon dioxide.

There are, it is stated, two distinct diastases, one of which liquefies the gelatinized starch, and the other effects its hydrolysis to the several fermentable sugars. The sugars in the "wort" are accompanied by nitrogenous substances (proteins), which are important, being essential to the yeast to enable it to perform its work of fermentation and for enhancing the flavour of the beer to be produced. Hops are boiled with the wort in order to give the required bitter character and to preserve the beer from undesirable subsequent fermentative changes. The strength and flavour of the beer admit of endless variation, strong beers containing more alcohol than mild ales, and substantial ones having more "body"—that is, being richer in malt extract.

In making English ordinary beer a yeast is used which rises to the top, whereas in "Lager" or bottom-fermentation beer making, a lower temperature is observed and the yeast sinks to the bottom, the latter process taking some eighteen to twenty-one days as against five or seven days for the former. Mild or sweet beers are sent out within a few days of brewing, but pale and bitter ales are kept for a longer period before distribution. The character of the water is of great importance, but the presence of sulphates (permanent hardness) is an essential factor in the brewing of pale ales, although soft waters are better for stout and porter.

Bacteria of the *Acetobacter R.* type are frequently present in beers, and exposure to air always results in formation of acidity, whilst curtailment of air supply enables them to produce mucilage.

The purity of the yeast is of great importance, and much care is taken in scientific brewing to prepare pure cultures, so as to avoid the presence in the beer of those undesirable substances which are produced by wild yeasts and other associated ferments.

Brewers' grains have a considerable food value, containing when dry some 20 to about 34 per cent. albuminoids and 30 to 50 per cent. digestible carbohydrates, while the squeezings from the wet grains, containing solids in suspension, have a higher value than the grains themselves. The average percentage composition of barley (pale ale dried grains) has been given as follows: Moisture 14.9, oil 1.5, proteins 8.6, digestible carbohydrates 67.9, mineral matter 2.6, woody fibre 4.5. Barley yields about one-third of its weight of dried grains.

Sodium hypochlorite or bleaching powder solution can be usefully

employed for the disinfection of brewery pipes and utensils. Beer casks are best treated with gaseous sulphur dioxide or calcium bisulphite after washing.

(See *Brewing and Malting*, by J. Ross-Mackenzie and H. G. Wright (Crosby Lockwood and Son, London); Hops, Malt, Ropiness, and Starch.)

**BEER'S LAW** — The absorption of light by an absorbing solution depends upon the thickness,  $d$ , of the solution, and upon the molecular concentration,  $c$ , of the absorbing material in the thickness of the solution under examination. Thus,  $I_d = I_i \times e^{-kcd}$  (Beer's Law), where  $I_i$  is the intensity of the initial light,  $I_d$  the intensity of the light after passing through a distance  $d$  in the solution,  $e$  the logarithmic constant (2.72), and  $k$  the absorption coefficient. (See *Theories of Organic Chemistry*, by F. Henrich (John Wiley and Sons, Inc., New York), p. 387 *et seq.*; and Photometry.)

**BEE SWAX** — See Waxes.

"**BEETLE**" — See "Beetl."

**BEET-SUGAR** — See Sugar.

**BÉGASSE** — See Sugar.

**BELLADONNA (Deadly Nightshade)** — The plant of *Atropa Belladonna* (Solanaceæ), cultivated in England and Germany. Indian Belladonna is obtained from *Atropa acuminata*. Both the herb and the root are used for medicinal preparations, the principal constituent being an alkaloid, *l*-hyoscyamine,  $C_{17}H_{23}O_3N$ , associated with a little atropine (*dl*-hyoscyamine). Belladonna herb contains from 0.3 to 1.0 per cent. of total alkaloids, some of which consist of volatile bases including methyl pyroline and pyrrolidine. Preparations of belladonna are used in medicine in the form of extracts, tinctures, and plasters to check excessive secretion and to allay inflammation. (See "Indian Belladonna," by C. E. Corfield in *Quart. J. Pharm.*, **16**, 108 (1943); and Rowson, in *Chem. Drug.*, **140**, 150 (1943); Atropine, and Henbane.)

**BELLITE** — See Explosives.

**BELL-METAL** — See Alloys.

"**BENADRYL**" (Diphenhydramine Hydrochloride) ( $C_{17}H_{21}ON$ ) — A complex compound, namely,  $\beta$ -di-methylaminoethylbenzhydryl ether, being one of a series of drugs antagonizing the action of histamine, used in medicine for the treatment of allergic conditions such as hay-fever. It is used in the form of its hydrochloride.

**BEN OIL** — From the seeds of *Moringa pterygosperma*, found in Egypt, Abyssinia, Syria, etc.; recommended as a lubricant for fine machinery. The seeds yield about 48.8 per cent. kernel, which yields over 50 per cent. oil of sp. gr. at 15/15° C. 0.9151; ref. ind. at 40° C. 1.461; sap. v. 188.2; i.v. (Wijs) 71.2.

"**BENGAL FIRE**" — A mixture of realgar (arsenic disulphide), sulphur, and nitre (potassium nitrate).

**BENTONITE** (*Willkitite*) — The name given to a group of colloidal clay-like materials or hydrated silicates of aluminium of variable composition found in Wyoming, South Carolina, and other parts of the U.S.A., as also in British Columbia, and Canada; usually dark, dull, powdery, but waxy on freshly cut surfaces, and varying in colour from yellowish-green to nearly black; products of the changes of volcanic ash; characterized by an alkaline oxide and alkaline earth content of from 5 to 11 per cent.; and possess high adsorptive power. The bentonite clays are the most adsorptive of all varieties, and some of them will adsorb more than three times their own weight of water, swelling up and producing a jelly-like mass. Analyses show a content of from 54 to nearly 80 per cent. silica ( $\text{SiO}_2$ ) and 12 to 27 per cent. alumina ( $\text{Al}_2\text{O}_3$ ), together with small amounts of  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ .

Bentonite has been used in making the plaster known as "Antiphlogistine" and as an incorporated ingredient of certain soaps to the extent of from 25 to 30 per cent.; as also a "filler" for felt, paper, etc., as a substitute for fuller's earth in oil bleaching, as a good emulsifier for certain oils, and for the de-inking of paper. It is announced that a process has been invented to transform bentonite into artificial mica.

*Ardmonite* is the name given to a special variety of clay found at Admore in South Dakota. *Taylorite* is an old disused name for bentonite. The variety used in the paper and oil industries is variously known as *Halloysite* and *Otalite*, and comes from South California, being first dried and then treated with acid before use.

**BENZALDEHYDE** ( $\text{C}_6\text{H}_5\text{CHO}$ ) — A colourless liquid of high refractive character and almond-like odour, soluble in alcohol and ether, of sp. gr. of 1.05 and b.p.  $179^\circ\text{C}$ . Artificial oil of bitter almonds (benzaldehyde) is prepared from benzyl chloride ( $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ ) by heating it with water and cupric nitrate, whereby it is hydrolysed and oxidized to benzaldehyde, or industrially by passing the vapour of toluene mixed with air over vanadium pentoxide catalyst at a carefully regulated temperature. It is used in perfumery, in dyestuffs, and for flavouring purposes. (See Almond Oil, and Glycosides.)

**BENZAMIDE** — See Amides.

**BENZAMINE HYDROCHLORIDE** (*Betacaine Hydrochloride*, *Eucaine Hydrochloride*) ( $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N.HCl}$ ) — The hydrochloride of 4-benzoyloxy-2,2,6-trimethylpiperidine, a white crystalline compound, soluble in water (1 in 30) and in 90 per cent. alcohol (1 in 35), m.p. about  $268^\circ\text{C}$ . Used in medicine as a local anæsthetic.

**BENZAMINE LACTATE** (*Betacaine Lactate*, *Eucaine Lactate*) ( $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N.C}_3\text{H}_5\text{O}_3$ ) — A white crystalline salt, soluble in water (1 in 5) and in 90 per cent. alcohol (1 in 8), m.p.  $152^\circ$  to  $156^\circ\text{C}$ . A local anæsthetic, possessing half the toxicity of cocaine, slower in action and producing more prolonged anæsthesia.

**BENZANILIDE** ( $\text{C}_6\text{H}_5\text{CO.NHC}_6\text{H}_5$ ), m.p.  $158^\circ\text{C}$ ., distils unchanged and is used in pencils to ascertain if the iron is too hot before ironing clothes, as it leaves a white mark on the sole of the iron if not hot enough for use.

“**BENZEDRINE**” — See Amphetamine.

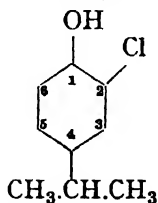
**BENZENE** ( $C_6H_6$ ) — A liquid hydrocarbon of cyclic structure, sp. gr. of 0.878, m.p.  $5.5^\circ C.$ , b.p.  $80.1^\circ C.$ , obtained from the products of the distillation of coal and from the cracking of certain light-oils. It is colourless, inflammable, of characteristic odour, soluble in alcohol and ether, and can be prepared in a crystalline state by freezing the pure liquid. It is an excellent solvent of resins and fats, and in crude form (benzol) is extensively used as a fuel for motors. It is a primary material in the manufacture of aniline dyes and many other organic compounds. Its toxicity as a powerful destroyer of blood corpuscles is a factor that should always be borne in mind by users. Benzene free from thiophen is required for use in certain syntheses.

Benzene is the initial member of the benzene series of hydrocarbons, and can be obtained pure by distillation of a mixture of benzoic acid and lime. It is the chief constituent of the commercial product known as “solvent naphtha.”

All the hydrogen atoms in benzene are replaceable by other atoms or groups, and among the many substitution or derived products are (1) monochlorobenzene (chlorobenzene) ( $C_6H_5Cl$ ), a liquid used in making picric acid and dyestuffs, (2) *para*-dichlorobenzene ( $C_6H_4Cl_2$ ) (1, 4) used as a repellant for clothes moths, (3) nitrobenzene ( $C_6H_5NO_2$ ) (see same), (4) *meta*-dinitrobenzene ( $C_6H_4(NO_2)_2$ ) (1, 3), and (5) benzenesulphonic acid ( $C_6H_5.SO_2OH$ ) (see same). By carefully controlled partial oxidation, using catalysts, maleic and fumaric acids (which are useful in the dyeing and tanning industries) are produced, and by further oxidation with potassium permanganate it is slowly converted into formic and oxalic acids. (See *Physical Constants of Mononuclear Aromatic Hydrocarbons*, by Gustav Egloff and A. V. Grosse (Universal Oil Products Booklet No. 217, 1938) for data on 181 compounds; Benzol, and Hydrocarbons.)

**BENZENE HEXACHLORIDE** — See “Gammexane.”

**BENZENE RING** — This is the name given to the hexagon, not necessarily regular, but always drawn with each side parallel to the opposite one, used to represent benzene ( $C_6H_6$ ) and its substitution products. The hydrogen atoms are not usually drawn, only the substituents being indicated, thus, 2-chloro-4-isopropyl phenol is



The ring is numbered in a clockwise direction starting from any point, but the numbers are not usually shown in diagrams. The distance between the centres of neighbouring C-atoms is  $1.39 \pm 0.02$  angstrom units, a distance intermediate between that of neighbouring C-atoms

in paraffin hydrocarbons ( $1.55 \pm 0.03$ ) and in olefin hydrocarbons ( $1.34 \pm 0.02$ ), and believed to be due to resonance in the molecule. H to C similar distances are  $1.08 \pm 0.04$ , and the whole molecule lies in a plane as shown by electron-diffraction studies.

**BENZENESULPHONIC ACID (Mono)** ( $\text{C}_6\text{H}_5\cdot\text{SO}_2\text{OH}$ ) — A crystalline deliquescent intermediate of m.p. about  $65^\circ\text{C}$ ., soluble in water, alcohol, and ether, prepared by the sulphonation of benzene.

**BENZIDINE (Benzidine Base)** ( $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ ) — A derivative of diphenyl, a greyish-yellow, crystalline, basic body of m.p.  $122^\circ\text{C}$ . and b.p.  $400^\circ\text{C}$ . (740 mm.). It is soluble in alcohol, ether, and hot water, and is of importance in the colour industry, because the so-called "substantive" colours which dye unmordanted cotton directly can be obtained from it. Congo red and chrysamine belong to this group of colours. Benzidine is prepared by a reduction process from nitrobenzene in alkaline solution by means of zinc dust; also by the electrolysis of nitrobenzene followed by distillation; stronger reducing agents produce aniline. Hydrazobenzene ( $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ ) the product of the alkaline reduction of nitrobenzene is transformed into benzidine by the action of strong acids.

**BENZIL (Dibenzoyl)** ( $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ ) — A yellow crystalline body of m.p.  $95^\circ\text{C}$ ., produced by oxidation of benzoin with nitric acid; readily nitrated. Dinitrobenzil ( $\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_6\text{H}_4(\text{NO}_2)_2$ ) is a pale yellow crystalline body soluble in benzene, chloroform, and acetone.

**BENZINE** is not synonymous with benzene, but a name usually given to a mixture of aliphatic hydrocarbons boiling between  $120^\circ$  and  $150^\circ\text{C}$ . Persian benzine contains only 2.3 per cent. benzene, and this is associated with many other hydrocarbons. It is used as motor spirit, and solvent. (See Motor Spirit, and Petroleum.)

**BENZOCAINE** ( $\text{C}_9\text{H}_{11}\text{O}_2\text{N}$ ) — A white crystalline substance, namely, ethyl *p*-aminobenzoate; sparingly soluble in water, soluble in alcohol, ether, and chloroform; m.p.  $90^\circ$  to  $91^\circ\text{C}$ .; used in medicine as a surface anæsthetic.

**BENZOIC ACID** ( $\text{C}_6\text{H}_5\text{COOH}$ ) — A colourless, crystalline compound, slightly soluble in water, soluble in alcohol and ether; sublimes readily at  $100^\circ\text{C}$ .; m.p.  $121^\circ$  to  $122^\circ\text{C}$ . and b.p.  $250^\circ\text{C}$ . It is prepared synthetically by chlorination of toluene, hydrolysing the resulting benzotrichloride ( $\text{C}_6\text{H}_5\cdot\text{CCl}_3$ ) by heating under pressure with calcium hydroxide and distilling off the benzoic acid. It can also be obtained from gum benzoin by sublimation and occurs naturally in many resins such as tolu and dragon's blood. It has antiseptic properties and is used in the tobacco industry, perfumery, and in medicine.

**BENZOIC ANHYDRIDE** ( $(\text{C}_6\text{H}_5\cdot\text{CO})_2\text{O}$ ) — A crystalline substance, m.p.  $42^\circ\text{C}$ ., the anhydride of benzoic acid, into which it is converted by hot water or alkali.

**BENZOÏN** ( $\text{C}_6\text{H}_5\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ ) — Obtained in yellow crystals, m.p.  $134^\circ\text{C}$ ., by the action of a solution of potassium cyanide on benzaldehyde, with which substance it is polymeric. Nitric acid oxidizes it to benzil.

**BENZOÏN GUM** — See Gums and Resins.

**BENZOL** (Benzole, Solvent Naphtha) — Commercial product, containing benzene, toluene, xylene, and other hydrocarbons. It is a nearly colourless liquid of sp. gr. 0.878, b.p.  $80^\circ\text{C}$ ., soluble in alcohol and ether, obtained from the distillation of coal-tar and by scrubbing coal gas and coke-oven gas. Its production is favoured by use of high heat in roasting coal and light creosote oil or "tetralin" as liquid absorbent, while activated carbon, activated alumina, and silica gel are among the solid absorbents that can be alternatively used. Its vapour exercises toxic influence. The crude article is used as fuel for internal combustion engines. The so-called resinification of unrefined benzoles which occurs during storage is primarily dependent upon the initial autoxidation of the unsaturated hydrocarbons. The stabilization of crude benzol by the addition of small quantities of inhibitors has been studied with considerable success. (See Reports of the Joint Research Committee of the National Benzole Association and University of Leeds; *Motor Benzole, its Production and Use*, by Hoffert and Claxton (National Benzole Assoc., Ltd.); Benzene, Coal, Colloidal Silica, Motor Spirit, Naphtha, and Paints.)

**BENZONAPHTHOL**, or  $\beta$ -NAPHTHYL BENZOATE ( $\text{C}_6\text{H}_5\cdot\text{COOC}_{10}\text{H}_7$ ) — A white substance, m.p.  $107^\circ\text{C}$ ., soluble in hot alcohol and formerly used as an intestinal antiseptic.

**BENZOPHENONE** (Diphenyl Ketone) ( $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ ) — An aromatic ketone, has two forms in the solid state, melting at  $26^\circ$  and  $48^\circ\text{C}$ ., respectively. On melting either form, the liquid boils at  $306^\circ\text{C}$ .

**BENZOYL** — The radical group,  $\text{C}_6\text{H}_5\text{CO}$ —.

**BENZOYL PEROXIDE** ( $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{O}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ ) — A crystalline, explosive, oxidizing, and drying agent, soluble in dry toluene; m.p.  $106^\circ\text{C}$ . Sometimes used for bleaching flour.

**BENZYL** — The radical group,  $\text{C}_6\text{H}_5\text{CH}_2$ —.

**BENZYL ACETATE** ( $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{C}_2\text{H}_3\text{O}_2$ ) — Occurs in several essential oils, and is made from benzyl alcohol and acetic acid by action of strong sulphuric acid; sp. gr. 1.060, b.p.  $216^\circ\text{C}$ .; used in perfumery.

**BENZYL ALCOHOL** ( $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{OH}$ ) — A colourless aromatic alcohol of sp. gr. 1.05, b.p.  $206^\circ\text{C}$ ., ref. ind. 1.532, soluble in alcohol and ether, used in perfumery and made by the action of potassium hydroxide on benzaldehyde followed by distillation, or from toluene by chlorine gas while boiling. After purification by distillation, the resulting benzyl chloride is converted into benzyl alcohol by hydrolysis effected by steam in the presence of soda ash.

**BENZYLANILINE** ( $C_6H_5.NH.CH_2.C_6H_5$ ) — A crystalline intermediate used in the manufacture of certain dyestuffs, prepared from benzyl chloride and aniline; m.p.  $33^\circ C.$ ; b.p.  $310^\circ C.$

**BENZYL BENZOATE** ( $C_6H_5.COOCH_2.C_6H_5$ ) — Occurs naturally as a constituent of the balsams of Peru and Tolu and is prepared by esterifying benzyl alcohol with benzoic acid, or by interaction between sodium benzoate and benzyl chloride. It occurs as colourless crystals or as an oily liquid; b.p. about  $323^\circ C.$ ; sp. gr. 1.224. It is used in medicine, a 25 per cent. emulsion being applied to the skin for the treatment of scabies. It is also used in perfumery as a solvent for artificial musk.

**BENZYL CELLULOSE** — A base for lacquers, and enamels.

**BENZYL CHLORIDE** ( $C_6H_5.CH_2Cl$ ) — A colourless aromatic liquid, prepared (1) by chlorinating boiling toluene, or (2) by hydrogen chloride passed into a suspension of paraformaldehyde and anhydrous zinc chloride in benzene. A yield of 79 per cent. is claimed in the latter process (R. C. Fuson and C. H. McKeever, "Chlormethylation of Aromatic Compounds," in R. Adams, *Organic Reactions*, 1, 63–90, John Wiley and Sons, New York). It has sp. gr. 1.1027, and b.p.  $179^\circ C.$ , and used in the preparation of benzaldehyde, and certain dyes. (See Almond Oil, and Benzyl Alcohol.)

**BERBERINE** ( $C_{20}H_{21}O_4N.6H_2O$ ) — A yellow, crystalline alkaloid obtained from the bark of *Berberis vulgaris* and present also in the roots of *Hydrastis canadensis*; soluble in water, alcohol, and ether; m.p.  $144^\circ C.$  Berberine sulphate is used in medicine for the treatment of Oriental sore.

**BERGAMOT OIL** — The yellowish-green, limpid essential oil expressed from the peel of *Citrus Aurantium* (subsp. *bergamia*), which grows in South Europe (chiefly Calabria). The average yield from the fruit is stated to be 0.48 per cent. It contains 35 to 45 per cent. of linalyl acetate together with about 6 per cent. of free *l*-linalol, and various terpenes; sp. gr. 0.882 to 0.886 at  $15^\circ C.$ ; ref. ind. 1.464 to 1.467 at  $20^\circ C.$ ; opt. rot.  $+12^\circ$  to  $+24^\circ$ ; used in perfumery, and for flavouring toilet articles and sweetmeats.

**BERGINIZATION** — Bergius' process for fluidifying coal is briefly described under the subject of coal. According to one account, the crushed coal is mixed with half its weight of coke-oven tar from which the oils distilling below  $250^\circ C.$  have been removed, and there is incorporated in the pasty mass some 5 per cent. of its weight of hydrated iron oxide ("Luxmasse"), to act either as a catalyst or for the removal of hydrogen sulphide from the evolved gases. The resulting mixture, together with an equal weight of pebbles, is then heated by gas jets in a series of bombs rotating at a speed of 60 r.p.m. at  $460^\circ$  to  $490^\circ C.$ , while hydrogen gas is pumped in at a pressure of from 200 atmospheres gradually reduced to 60 atm.

It is stated that only coal the carbon content of which is lower than 85 per cent. (calculated on the ash-free product) is completely amen-

able to the process, while the presence of sulphur is more or less inimical. The black, tarry, liquefied product yields several fractions upon subsequent distillation between 60° and 300° C. (some 70 per cent. in all), the residue being pitch-like in character. The younger lignites contain more hydrogen than the older bituminous coals and are consequently more amenable to berginization. With certain varieties of coal it is possible to convert 90 per cent. of it into gas and benzine-soluble liquid (Ormandy).

According to Shatwell and Graham (1925), "clarain" and "durain" parts of coal absorb 3.36 to 3.60 per cent. hydrogen under high pressure at 400° to 436° C. in presence of phenol, but the "fusain" part is not affected by this process, the phenol appearing to act as a solvent of the hydrogenated products.

Berginization has been tested in respect of various oils and other materials. The German inferior brown coals yield by low temperature carbonization a crude oil from which, by hydrogenation, Diesel oil and motor spirit are obtained, but British coals are not so suitable. From a French source it has been reported that a metric ton of coal gives 200 kilograms of gas and from 400 to 500 kilograms of liquid, consisting of 25 per cent. phenol and 75 per cent. of a mixture resembling crude petroleum when heated (according to the nature of the coal) to from 400° to 450° C. in hydrogen at a pressure of 150 kilograms per sq. cm. From the mixture 80 kilograms of petrol can, it is added, be extracted, leaving a heavy oil unsuitable for cracking. (See Coal, Hydrogenation, Liquid Coal, and Liquid Fuel.)

**BERKELIUM** (Bk) — Element 97, announced in January, 1950, by S. G. Thompson, Albert Ghiorso, and Glenn T. Seaborg, of the University of California, Berkeley. Prepared by the irradiation of a minute quantity of americium with cyclotron alpha particles.

**BERYL** — See Beryllium.

**BERYLLIUM** (Be) and its Compounds — Atomic weight, 9.013 (1949).

See Elements for other data. Beryllium occurs in a number of minerals, including *beryl* (a double silicate of beryllium and aluminium ( $3\text{BeO}, \text{Al}_2\text{O}_3, 6\text{SiO}_2$ ), found in Ontario, Quebec, New Hampshire, Maine, Massachusetts, Connecticut, South Dakota, and other places), of crystal system No. 6 and sp. gr. 2.63 to 2.75, *chrysoberyl* ( $\text{BeAl}_2\text{O}_4$ ), and *phenacite* as ortho-silicate ( $\text{Be}_2\text{SiO}_4$ ). There are various types of beryls, varying in constitution from the formula usually assigned. Brazil is the principal exporting country.

Beryl is not appreciably attacked by acids, but suffers decomposition upon fusion with caustic potash; subsequent treatment with dilute sulphuric acid causes the precipitation of silica, and potash alum can be crystallized out, leaving beryllium sulphate in solution, from which the hydroxide can be prepared.

Beryllium is a steel-grey, fairly malleable, brittle, light density metal which cannot be drawn, rolled, or filed, nearly as hard as iron, but said to be ductile when quite pure. It resembles magnesium in some respects; is soluble in acids; when strongly heated is converted into

the oxide, and in its pulverulent form takes fire upon heating. The metal itself can be obtained by heating metallic sodium in the vapour of the chloride, also by the electrolysis of a fused mixture of sodium-beryllium fluoride and barium-beryllium fluoride at  $1,350^{\circ}\text{C}$ . The double fluoride of beryllium and sodium mixed with some barium fluoride can be used, and a still better mixture, according to Illig and others, is one of barium fluoride and beryllium oxyfluoride.

Beryllium is useful as a constituent of light-weight alloys, and a small quantity imparts strength to aluminium. It acts as a useful deoxidizer in copper castings, and in small proportions forms, with nickel and copper respectively, alloys resembling some of the bronzes. Its lightness and its m.p., which is higher than that of aluminium and magnesium, present advantages, but, so far, its cost tells against its extensive employment as an alloying metal. (See *Chemistry and Literature of Beryllium*, by C. L. Parsons (Reinhold Publishing Corp., New York); *Beryllium. Its Production and Application* (Reinhold Publishing Corp., New York); *Rarer Metals*, by Jack De Ment and H. C. Dake (Chemical Publishing Co., Brooklyn).)

**Beryllium Oxide** ( $\text{BeO}$ ) is a white infusible solid of sp. gr. 3.0, soluble in acids.

**Beryllium Chloride** ( $\text{BeCl}_2$ ) is obtained by heating the oxide with charcoal in a current of chlorine. It is a white, crystalline, volatile substance.

Many of its compounds, such as the fluorides ( $\text{BeF}$  and  $\text{BeF}_2$ ), chloride, bromide, sulphide, carbide, sulphate, nitrate, resemble the corresponding aluminium compounds in general character.

**BERZELIANITE** — A rare mineral, consisting of copper selenide associated with silver, thallium, and iron.

**B.E.S.A.** — British Engineering Standards Association, now the British Standards Institution (B.S.I.).

**BESSEMER PROCESS** — See Iron.

**BETAINE** ( $\text{C}_5\text{H}_{11}\text{O}_2\text{N}, \text{H}_2\text{O}$ ) — A colourless, inert, tasteless, crystalline, alkaloidal substance contained in molasses of beet-sugar. (See "Acidol.")

**BETA-NAPHTHOL** — See Naphthol (Beta).

**BETA PARTICLE** — See Electron.

**BETA-RAYS** — See Radioactivity.

**BETATRON** — An apparatus designed by Kerst and Serber in 1941 to impart high energy to electrons.

**BETEL** — A mixture of the leaves of the betel pepper, *Chavica betle* or *Piper betel* L. (indigenous to the E. Indian Archipelago and cultivated in India and Ceylon), with the dried ripe seeds of the *Areca catechu* or betel-nut palm; used by the natives of tropical Asia as a masticatory. (See Catechu.)

**BETRATA OIL** — The seeds of betrata (*Riciodendron mahafalense*) are stated to yield 44.64 per cent. of a pale golden oil which makes a good hard soap, and the residual cake is of good quality.

**BICHROMATES (Dichromates)** — See Chromium Compounds.

“ **BICHROME** ” — Trade name for potassium dichromate.

“ **BIDEFORD BLACK** ” — A mineral material containing, when mined, roughly about 30 per cent. carbon and 70 per cent. other substances, from which may be prepared, by suitable treatment, a product containing up to 74 per cent. carbon, very useful as a pigment, for use in connection with rubber and cement and the production of black flooring tiles, etc.

**BILE** is the secretion of the liver as discharged into the duodenum, and plays an important part in the process of food digestion. It is a viscid liquid of sp. gr. about 1.02 and yellowish-green colour (which becomes more yellow on dilution), owing its viscosity to the presence of a quantity of mucus derived from the gall-bladder. It consists of more than 90 per cent. water, but the biliary matters proper contain taurocholate and glycocholate of sodium, several colouring matters (the chief of which is bilirubin), also a small quantity of cholesterol, lecithin, and choline.

The bile acids are closely related to cholesterol ( $C_{27}H_{46}O$ ), and possess the same ring system as the sterols. All of them are derived from cholic acid ( $C_{24}H_{40}O_2$ ). The following table gives a list of the bile acids:

Name	Formula	M.P., °C.	Source
Lichocholeic acid (3-hydroxycholeic acid) .. .. .	$C_{24}H_{40}O_3$	186	Man, ox.
Deoxycholeic acid (3,12-dihydroxycholeic acid) .. .. .	$C_{24}H_{40}O_4$	172	Man, ox, goat, sheep.
Chenodeoxycholeic acid (3,7-dihydroxycholeic acid) .. .. .	„	196	Man, goose.
Hyodeoxycholeic acid (3,6-dihydroxycholeic acid) .. .. .	„	140	Pig.
Cholic acid (3,7,12-trihydroxycholeic acid) .. .. .	$C_{24}H_{40}O_5$	195	Man, ox, goat, sheep.
beta-Phocaecholic acid (3,7,23-trihydroxycholeic acid) .. .. .	„		

They occur in bile as salts of their amides with glycine or taurine, e.g., glycocholeic acid  $C_{24}H_{39}O_4(NH.CH_2.COOH)$ , which crystallizes in long needles, m.p. 133° C., freely soluble in hot water; and taurocholeic

acid ( $C_{24}H_{38}O_4(NH.CH_2.CH_2.SO_3H)$ ), both of which are hydrolysed into their constituents by prolonged boiling with alkali. Deoxycholic acid forms well-crystallized additive compounds with fatty acids, *e.g.*, 1-deoxycholic acid-8-palmitic acid, m.p.  $186^\circ C.$ , which was formerly called choleinic acid.

The relationship of cholesterol to the bile acids is shown by the fact that the same acid—cholanic acid—may be obtained from both.

The bile pigments are :

Bilirubin ( $C_{33}H_{36}O_6N_4$ ), the orange pigment of bile.

Mesoverdin ( $C_{33}H_{36}O_8N_8$ ), the green pigment of bile.

Mesobilirubinogen, formed by reduction of bilirubin.

Mesobilirubin, the brown pigment of urine.

Uteroverdin, the green pigment of egg-shells, of the placenta of the dog, and of the gall-stones of the ox.

See Rosenheim and Kay on "The Ring Systems of Sterols and Bile Acids" (*Chem. and Ind.*, **51**, 464, 954 (1932); **52**, 299 (1933)); I. M. Heilbron in *Chem. and Ind.*, **51**, 1061 (1932); report of discussion in *Chem. and Ind.*, **52**, 10 (1933); *Hematin Compounds and Bile Pigments*, by R. Lemberg and J. W. Legge (Interscience Publishers, New York).

"**BILOSELECTAN**" — See Pheniodol.

**BINDERS** — See Adhesives, Briquetting, and Cements.

**BINDING ENERGY** — The energy that must be introduced into the nucleus of an atom to cause it to release a nuclear particle such as a neutron. (See Nuclear Chemistry.)

**BIOCHEMISTRY** is the application of chemistry to biological material. The subject is concerned with composition of animals and plants, as well as their secretions and products derived from them. Biochemistry also includes the study of the normal and pathological processes which go on in living organisms, such as digestion, respiration, growth, reproduction, etc.

Many phases of biochemistry have been given specific names, such as physiological chemistry (animals), and phytochemistry (plants). More extended discussions of biochemical processes will be found under specific topics in this book, such as Amino-acids, Bacteria, Bile, Blood, Bones, Feeding Stuffs, Foods, Proteins, Respiration, Urine, Vitamins.

There are many excellent books on the subject of biochemistry. Some of them are : *Outlines of Biochemistry*, by Gortner (John Wiley and Sons, New York); *Physiological Chemistry*, by Matthews (Baillière, Tindall and Cox, London); *Introduction to Physiological Chemistry*, by Bodansky (Chapman and Hall, London); *An Introduction to Biochemistry*, by R. J. Williams (D. Van Nostrand Co., New York); *Fundamentals of Biochemistry*, by T. R. Parsons (W. Heffer and Sons, Cambridge); *Annual Reviews of Biochemistry* (Stanford Univ. Press); Reports on Biochemistry in *Annual Reports of the Progress of Chemistry* (Chemical Society, London).

**BIOTIN (Bios)** — See Vitamins.

**BIOTITE (Black Mica)**  $(\text{H}_2\text{K}(\text{Mg},\text{Fe})_3(\text{Al},\text{Fe})(\text{SiO}_4)_3)$  — A micaceous orthosilicate of crystal system No. 5, and sp. gr. 2·7 to 3·0, cleaving into thin elastic leaves. (See Mica.)

**BIPHENYL** — Same as Diphenyl.

**BISMARCK BROWN (Triaminoazobenzene Hydrochloride)**  $(\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_3(\text{NH}_2)_2\cdot\text{HCl})$  — A reddish-brown crystalline basic bisazo dye used for leather, furniture, etc.

**BISMUTH (Bi) and its Compounds** — Atomic weight, 209·00. See Elements for other data. Bismuth occurs in nature (associated with traces of sulphur, arsenic, and tellurium) mainly in the metallic state; also combined with oxygen as *bismuth ochre* ( $\text{Bi}_2\text{O}_3$ ), of crystal system No. 4, and sp. gr. 4·36; with sulphur as *bismuth glance* ( $\text{Bi}_2\text{S}_3$ ), and with tellurium as *tetradymite* (a natural telluride ( $\text{Bi}_2\text{Te}_2\text{S}$ ) found in Arizona, California, etc.). It is also found as *bismuth nickel* ( $\text{Bi}_2\text{S}_3$  with NiS); as *bismuthinite* (a sulphide ( $\text{Bi}_2\text{S}_3$ ) occurring in association with gold in Rowan Co., N.C.); as *bismuth-gold* ( $\text{Au}_2\text{Bi}$ ) at Maldon, Victoria; as a natural basic carbonate named *bismutite* (of crystal system No. 4, found in auriferous quartz in the Transvaal), which yields about 90 per cent. of the oxide  $\text{Bi}_2\text{O}_3$ ; also in association with antimony in *kobellite*, *hauchecornite*, and *chiviatite*. Bismuth ochre and bismutite are regarded as secondary minerals derived from the primary bismuthinite and bismuth.

#### BISMUTH METAL, WORLD PRODUCTION

Annual average for the three-year period 1943–1945, since data for 1937–1939 not available

Data arranged and rounded off by the Editor.

Country	Bismuth Metal Metric Tons				
France .. .. .	..	..	..	10	
Spain .. .. .	..	..	..	10	
				—	20
U.S.A. .. .. .	..	..	..	500*	
Mexico .. .. .	..	..	..	170	
Canada .. .. .	..	..	..	110	
				—	780
Peru .. .. .	..	..	..	400	
Argentina .. .. .	..	..	..	20	
Bolivia .. .. .	..	..	..	10	
				—	430
Sum of above .. .. .	..	..	..		1,230

WORLD PRODUCTION, approximately the above.

\* Estimated.

Bismuth is a lustrous, white, brittle metal of a reddish tinge, obtainable in beautiful crystals, and forms alloys with other metals, of which one of the best known is *Wood's fusible metal*, which melts at  $60.5^{\circ}\text{C}$ . (See Alloys.) Bismuth amalgam is used for the silvering of mirrors. The crude metal contains sulphur, arsenic, antimony, copper, nickel, cobalt, silver, gold, lead, and iron; the sulphur and arsenic can be removed by fusion with potassium nitrate and the other impurities by special treatment. The pure metal is obtained by dissolving the crude material in nitric acid, precipitating the bismuth as basic nitrate by addition of water, and reduction with black flux or a mixture of coal, iron, and flux.

Among its compounds are two **chlorides** ( $\text{BiCl}_3$  and  $\text{BiCl}_4$ ), and four **oxides** (see article on Oxides), of which the trioxide ( $\text{Bi}_2\text{O}_3$ ) is of commercial importance; this is a yellowish insoluble powder of sp. gr. 8.2, prepared by heating the carbonate or nitrate, and is used to replace lead oxide in the manufacture of crystal glass. When acted upon by acids the oxides give salts, including bismuth **nitrate** ( $\text{Bi}(\text{NO}_3)_3$ ), soluble in alcohol but decomposed by water forming bismuth subnitrate, and bismuth **sulphate** ( $\text{Bi}_2(\text{SO}_4)_3$ ).

The **carbonate** as ordinarily prepared by the interaction of ammonium or sodium carbonate and a solution of bismuth nitrate is a mixture of carbonate and bicarbonate, and the precautions to be observed in order to obtain a light precipitate for medicinal use are described by A. J. Jones (*Chemist and Druggist*, August 1, 1925).

**Bismuth Trichloride** ( $\text{BiCl}_3$ ) is a white, crystalline, deliquescent substance, soluble in acids, but decomposed by water forming oxychloride, and employed for fireproofing inflammable materials used for waterproofing.

**Bismuth Subnitrate** ( $(\text{BiO})\text{NO}_3 \cdot \text{H}_2\text{O}$ ) is a heavy white powder insoluble in water; used in medicine and in preparing enamels, fluxes, and cosmetics, made by adding bismuth nitrate to water.

**Bismuth Sulphide** ( $\text{Bi}_2\text{S}_3$ ) is a black insoluble solid, made by interaction of bismuth salt solution and hydrogen sulphide or soluble sulphide.

**Bismuth Chromate** ( $\text{Bi}_2\text{O}_3 \cdot 2\text{CrO}_3$ ) is a yellow amorphous substance, insoluble in water, used as a pigment.

**Bismuth Subgallate (Bismuth Oxygallate)** — A yellow, basic, insoluble salt prepared by interaction between freshly precipitated bismuth hydroxide and gallic acid, used in medicine as an antiseptic astringent dressing.

The bismuth compounds are for the most part insoluble in water, and include many organo-derivatives. Among others used in medicine are subnitrate, subcarbonate ( $\text{Bi}_2\text{O}_3 \cdot \text{CO}_2 \cdot \text{H}_2\text{O}$ ), citrate ( $\text{Bi}_6\text{C}_6\text{H}_5\text{O}_7$ ), betanaphtholate (orphenol) ( $\text{Bi}(\text{C}_{10}\text{H}_6\text{OH})_3$ ), salicylate ( $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)_3 \cdot 4\text{H}_2\text{O}$ ), subsalicylate ( $\text{Bi}(\text{C}_7\text{H}_5\text{O}_3)_3\text{Bi}_2\text{O}_3$ ), and tribromophenylate (xeroform) ( $\text{Bi}_2\text{O}_3(\text{C}_6\text{H}_2\text{Br}_3\text{OH})$ ).

**BISMUTITE** — See Bismuth.

**"BISTRE"** — A dark brown pigment made from wood soot or peat smoke, and used as China ink.

**BISULPHITES** — See Sulphites.

**BITTER ORANGE PEEL** — The outer part of the pericarp of the fruit *Citrus Aurantium*, which is cultivated chiefly in Southern Spain and Sicily. It contains a volatile oil and a bitter, glycosidal substance called aurantiamarin. Both the fresh and dried peel are used in pharmacy for the preparation of tinctures and infusions having bitter and carminative properties.

**BITTERN** — The mother-liquor of sea-water left after crystallization of its salts.

**BITTERS** — Vegetable extracts having bitter properties, such as quassia, from quassia wood; wormwood, from the herb of that name; aloe, from the juice of the plant; angostura, from bark; orange, from the dried bitter orange peel; acorus, from the root of the common sweet flag; cascarilla, from bark; camomile, from the flowers; colocynth, from the fruit (*Citrullus colocynthis*); gentian, from gentian root. They are used in medicine to stimulate the appetite.

**BITUMEN** — See Asphalt, Emulsions, and Tar.

**"BITURAL"** — A bitumen-like material made in Australia from vertical retort tar by polymerization of its unsaturated hydrocarbon content. It is prepared by digesting a mixture of formaldehyde solution with ammonia of sp. gr. 0.88 and the tar at 150° F. for some hours, after which it is subjected to the passage of hot air. Formaldehyde condensation products are thus formed with the phenols, cresols, and xylois of the tar. The gummy product can be made of any desired consistency and has proved to be a very useful material resembling the softer grades of bitumen.

**BIURET** ( $\text{HN}(\text{CONH}_2)_2$ ) — A white solid, of m.p. 192° C. with decomposition, soluble in water and in alcohol, and crystallizes as needles from solution in alcohol. A solution of biuret in water shows a violet colour when treated with very dilute copper sulphate solution and then with sodium hydroxide solution.

**BLACK ASH** — The crude sodium carbonate as made by the old Leblanc process. (See Sodium (Carbonate).)

**BLACK-BAND** — See Iron.

**BLACK DAMMAR** — See Gums and Resins.

**BLACK-DAMP** — See Carbon Oxides.

**BLACKING** is commonly made from bone-black, sugar, and oil, with the addition sometimes of a little vinegar or strong sulphuric acid; there are, however, many recipes.

**BLACK-LEAD** — See Carbon.

**BLACKSTRAP** — See Molasses.

**"BLADAN"** — See Tetraethyl Pyrophosphate.

**BLANC FIXE** — See Barium Sulphate.

**BLEACHING** — An operation effected by oxidation or “reduction” of colouring matters to colourless ones, largely employed in the arts, a number of chemical agents being used therefor.

Bleaching-powder is used on a large scale, the materials to be bleached, such as calicoes and other fabrics, rags for paper-making, etc., being first steeped in a dilute solution (2 to 2½ per cent. strength) of the bleaching-powder and then in dilute acid. In the case of calico, the fabric is first of all well washed, and boiled successively with lime-water, much dilute sulphuric acid, and weak caustic soda, to remove the weavers' dressing, grease and resinous materials. Great care has to be taken in bleaching cloths having coloured strips so as to leave them unaffected, the process calling for scientific attention.

Hypochlorous acid, which may be said to act in the same way (calcium hypochlorite being the active principle of bleaching-powder), also serves the same purposes, readily giving up oxygen. It undergoes rapid decomposition on exposure to the air. At one time, particularly in France, a solution of sodium hypochlorite was extensively used for bleaching, being prepared under the name of *Eau de Javel*.

Liquefied chlorine has been much used for bleaching purposes in recent years, the Mathiesen system being based upon the vaporization of the liquid chlorine in a leaden coil immersed in the tank in which the bleaching solution is prepared.

It has been shown that cotton and linen contain two kinds of colouring matter, one which predominates in American cotton, and another which predominates in linen; and while the former is rapidly bleached by chlorine and more slowly by hypochlorous acid, the latter is quite unaffected, but is most readily bleached by a mixture containing free chlorine or hypochlorous acid along with hypochlorite.

Sulphur dioxide also exhibits powerful bleaching effects, and is largely used for bleaching straw, woollen and silk goods, isinglass, sponge, and other articles which would be injured by the use of chlorine compounds. To effect this, they have to be moistened and exposed to its fumes as generated by burning sulphur or, alternatively, treated with a dilute solution of the gas dissolved in water (sulphurous acid).

Sodium percarbonate gives 120 to 130 grams of active oxygen per kilogram, liberating it with regularity, and can be employed in respect of all fabrics to the extent of about 1.5 to 2 per cent. on the weight of the fabric to be bleached without the use of other agents.

Hydrogen peroxide is a very valuable bleaching agent, readily parting with its second constituent atom of oxygen, and has the great advantage of being perfectly innocuous to operators and goods. It is largely used in respect of delicate fabrics, straw goods, human hair, ivory, etc. The presence of alkaline silicate of sodium increases the efficiency of both hydrogen peroxide and hypochlorite solutions. (See Hydrogen dioxide.)

Potassium permanganate and other oxidizing agents are also used for some bleaching purposes.

**BLEACHING-POWDER** — See Calcium (Hypochlorite).

**BLLENDE** — Antimony blende (see Antimony), and Zinc blende (see Sphalerite, and Zinc).

**BLOOD** is built up from the digested food, and serves to supply all parts of the organism with fresh nutrient materials to replace those worn out by the processes of life, and it also dissolves and carries away some of the excretory products. It is slightly alkaline in reaction ( $pH$  7.35 to 7.5), sp. gr. 1.055 to 1.062, and its temperature in the living body is about  $37^{\circ}C$ . ( $98.5^{\circ}F$ ). It is by the medium of the blood that the great process of oxidation through respiration is effected. Besides the other smaller chemical differences between arterial and venous blood there is the greater one in the degree of oxidation, which is dependent upon the oxygen-carrying capacity of the red colouring matter (hæmoglobin), which contains iron, and consists of a combination of hæmatine ( $C_{32}H_{32}FeO_6N_4$ ) with a certain albuminous substance (globin). The arterial (aerated) blood carries oxygen into the system, whereas the venous blood is loaded with carbon dioxide and other impurities, which are set free in the lungs where the blood is renewed with its new supply of oxygen. Blood contains seralbumin, fibrin, and globulin in solution, together with a great number of other substances more or less definitely ascertained, in addition to its saline constituents. The clotting of blood is accompanied by an enzyme found therein named thrombin. The serum is that part of the blood which remains liquid after the coagulation of the fibrin which entangles in its meshes (clot) the blood corpuscles. Its content of seralbumin is completely separated (coagulated) by adding a little acetic acid and boiling. The liquid which forms in a blister is a familiar example of serum.

Blood-stains are identified by moistening with a freshly made solution of guaiacum resin in alcohol, and adding a drop of a solution of ether containing 1.2 per cent. hydrogen peroxide, when a blue colour is developed; or by combined chemical and fluorescent test by adding strong sulphuric acid, followed by excess of ammonium hydroxide. The fluorescent test is made both on the sulphuric acid and on the ammonium hydroxide media. The change from yellow-red fluorescence of the acid test material to carmine fluorescence of the hydroxide test material is stated to be a specific test for blood. (See F. W. Martin on "Ultra-Violet Rays in Criminal Investigation" (*Police Journal*, 7, No. 4 (1934).) (See Fibrin, Kjeldahl Process, Phagocytes, and Serum.)

**BLOOD ALBUMIN (Seralbumin)** — Is prepared from the serum of the blood of animals, and finds use in commerce in connection with printing colours on calico fabrics, also in the leather and other trades, and as a clarifying agent. It is contained in blood to the extent of about 0.08 per cent., the serum itself amounting to about 48.16 per cent.

**BLOOD-STONE** — A name given in common to a variety of jasper (native silica,  $SiO_2$ ), and to a kind of red hematite.

**BLOOM** — The fluorescence of petroleum and of rosin oils; the dulling of a varnish film; the exudation sometimes found on vulcanized rubber,

usually due to the separation of tiny particles of sulphur ; the deposit on leather caused by enzymes naturally present in some vegetable tanning materials, or by micro-organisms.

**BLOWN OIL** — See Linseed Oil, Oils, and Varnishes.

**BLUBBER OIL** — See Fish Oils.

**BLUE GAS**—Same as Water Gas, which see.

**BLUE STONE (Blue Vitriol)** — Common names for copper sulphate.

**" BLUE VERDITER "** — Trade name for basic cupric carbonate.

**BLUSHING** — The separation of cellulose ester from a lacquer film of the same, due to condensation of water from the air caused by the cooling of the film by rapid evaporation of the solvent.

**" BOBBINITE "** — A permitted explosive for use in safety-lamp mines. (See " Eversoft.")

**BOG-IRON ORE (Limonite)** — See Iron.

**BOHR'S THEORY** — In an attempt to explain the energy relations of the electrons in the structure of the atom, Bohr in 1913 made the startling suggestion that an electron always moved in a closed orbit (energy level) and as long as it did so there was no absorption or emission of energy as radiation. He postulated that an electron can have acceleration and yet not radiate energy. More than one stable state was considered to be possible for any electron, each being termed a stationary state or energy level. Thus, an electron can exist in energy level  $E_1$  or  $E_2$  and as long as it does so it will not absorb or emit energy as radiation, but if the electron transfers from energy level  $E_1$  to energy level  $E_2$  monochromatic radiation is emitted or absorbed in accordance with the equation

$$E_2 - E_1 = \epsilon = h\nu$$

where  $\epsilon$  is the quantum of energy of the radiation,  $h$  is Planck's constant, and  $\nu$  is the frequency of the radiation in reciprocal seconds.

Bohr assumed that the electrons revolve around the nucleus in elliptical orbits and that the centrifugal force of the electron is equal to the force of the electrostatic attraction between the electron and the nucleus. He further assumed that the motion of the electron was quantized and that instead of an infinite number of energy levels there is only a restricted number with properties represented by a function of the quantum number  $n$ , where  $n$  is an integer 1, 2, 3, 4, etc. Bohr was able to correlate the energy emitted when the electrons in an excited element changed energy levels with the spectral lines of that element by means of derived mathematical formulæ. Bohr's formula was so successful in calculating the lines of the hydrogen spectrum with exactness that the model on which it was based was generally accepted.

The Bohr concept is essentially pictorial, giving physical significance to the electron as a particle moving in one of a series of possible orbits ; however, modern quantum mechanics or wave mechanics has to regard the atom as a purely mathematical concept without requiring any definite model as a basis for the calculations.

**BOILED OIL** — See Linseed Oil, Varnishes, and Oils.

**BOILING POINT** (See Elements for data for individual elements) — If heat is applied to a pure liquid in an open container the temperature rises until a continuous flow of vapour bubbles formed in the liquid breaks through the surface, at which time the temperature remains constant and the liquid is said to boil. This temperature is called the boiling temperature of the liquid.

A consideration of the conditions necessary to maintain a bubble in a liquid will give a better understanding of this phenomenon.

If a bubble is to be maintained in a liquid, as just suggested, the pressure of the vapour in the bubble must be equal to the sum of the atmospheric and hydrostatic pressures over it, otherwise the bubble would collapse. If the vapour pressure in the bubble just exceeds the combined atmospheric and hydrostatic pressures the bubble will burst through the surface, and the liquid boils.

The boiling temperature of a liquid in an open vessel is dependent upon the accompanying atmospheric pressure. For example: water boils at 100° C. if the atmospheric pressure is 760 mm. of mercury, at 105° C. for 906 mm. of mercury, and at 95° C. for 634 mm. of mercury. Therefore, **the boiling point** of a liquid is the temperature at which its vapour pressure becomes *equal to 760 mm. of mercury pressure*.

Distillation under reduced pressure is boiling at a pressure less than 760 mm. of mercury, such as occurs on a high mountain or in a system attached to a vacuum pump in which cases the boiling temperature may be considerably below the boiling point.

Pressure cooking is boiling at pressures greater than 760 mm. of mercury as occurs in a sealed container where the vapour of the liquid cannot escape and thus increases the pressure against which the bubbles in the liquid must operate. This causes the boiling temperature to exceed the boiling point of the liquid.

Since a non-volatile solute reduces the vapour pressure of a liquid solvent, the resulting solution will not boil until a temperature higher than the boiling point of the pure liquid solvent has been reached. Thus, a one molal sugar-water (342 grams of  $C_{12}H_{22}O_{11}$  in 1000 grams of water) solution boils at 100.52° C.

A solution made up of two volatile liquids will have a boiling point at a temperature either greater than the boiling point of the higher boiling liquid, or at a temperature lower than the boiling point of the lowest boiling liquid, or at a temperature between the boiling points of the two liquids depending upon the particular composition of the solution and the type of solution that results upon mixing the two liquids. (See Evaporation, Heat (Thermochemical Aspects), and Vapour Pressure.)

**BOLE** — Various sorts of coloured clays. Armenian bole is of bright red colour; other kinds are yellow or yellowish-red. (See Ochres, and Sienna.)

**BONE-BLACK** (Bone-Char) — An impalpable form of carbon prepared by burning bones, and subsequently dissolving out the calcium

and other mineral salts by acid applications. The burnt residue before the treatment contains as chief constituents some 10 per cent. carbon finely disseminated throughout a mixture of about 80 per cent. calcium phosphate and about 10 per cent. other mineral matter, and when thus purified is of importance for use in sugar refining and decolourizing various liquids. It appears that the alkaline constituents of the char exert a considerable influence on adsorption of ash from sugar solutions. (See Bones, and Carbon.)

**BONE FAT** is reported to have a sp. gr. at 50°/30° C. of 0.9009 to 0.9034, m.p. 44° to 45° C., solidification-point 32.60 to 33.8° C., sap. v. 189.6 to 195.2, and i.v. (Hanus) 49.1 to 51.6. It is very similar to marrow fat, and yields 19 to 21 per cent. stearic acid, 20 to 21 per cent. palmitic acid, 53 to 59 per cent. oleic acid, and 5 to 10 per cent. glycerol.

**BONE-MEAL** — See Phosphorus.

**BONE-OIL** — See Dippel's Oil.

**BONES** — Dry bones contain about 30 per cent. of ossein, which, when dissolved in water, yields gelatine, and the average composition of dry bone after degreasing is: fat 6 per cent., ossein 28 per cent., calcium phosphate 56 per cent., calcium carbonate 8 per cent., magnesium phosphate 1 per cent., and calcium fluoride 1 per cent. After defatting and extraction of the mineral constituents by action of acids the ossein is left, or ossein may be obtained by cooking the defatted bones in autoclaves under pressure. Glue is prepared from the exuded ossein. (See Glue.)

**Bone-ash** contains about 87 per cent. calcium phosphate, 9 per cent. calcium carbonate, 3 per cent. calcium fluoride, and 1.7 per cent. magnesium phosphate. It is used in assaying and some industrial applications. (See *Bone Products and Manures*, by T. Lambert (Scott, Greenwood and Son, London); and Dentine.)

**BORACIC ACID** — See Boron Compounds.

**BORACITE** — See Boron.

**BORAX (Sodium Borate)** — See Boron.

**BORDEAUX MIXTURE** — An aqueous suspension prepared by mixing copper sulphate and lime together. It is an efficient fungicide, and is widely used to protect fruits and vegetables from disease. The concentrations and proportions of the reacting substances are varied, depending upon the application—a common formula used on potatoes calls for the use of 8 pounds each of copper sulphate and hydrated lime, in 100 gallons of water. The copper sulphate is dissolved in the water, and a suspension of lime added with agitation. The resulting product is a pale blue suspension, which is applied as a spray.

Bordeaux mixture has excellent adhesive properties, and remains on plant foliage for relatively long periods of time. The active principles are thought to be hydroxides and basic sulphates of copper. Dried Bordeaux preparations are available commercially. (See *Chemistry of Insecticides and Fungicides*, by D. E. H. Frear (D. Van Nostrand Co., New York).)

**BORNEOL, or BORNEOL CAMPHOR** ( $C_{10}H_{17}OH$ ) is a secondary alcohol, found in cavities of trunks of old trees of the order *Dryobalanops camphora* and as a constituent of spruce turpentine. It consists of small, colourless crystals (resembling ordinary camphor and pepper in odour), with a m.p.  $208^{\circ}C$ . and b.p.  $212^{\circ}C$ . It is nearly allied to ordinary camphor, from which it can be prepared by the action of nascent hydrogen— $C_{10}H_{16}O + 2H = C_{10}H_{17}OH$ —while borneol in hexane solution is stated to yield camphor by the action of ozone. It can be synthetically made from *alpha*-pinene. It is used in medicine and in the celluloid industry. (See Camphor.)

**BORNITE** — A mineral double sulphide of copper and iron ( $3Cu_2S, Fe_2S_3$ ) occurring in the U.S.A.

“**BOROCAINE**” — See Procaine.

**BORON (B) and its Compounds** — Atomic weight, 10.82. See Elements for other data. Boron occurs naturally in a number of combinations, one of the best known being *tincal*, a crude borate of sodium or *borax* ( $Na_2B_4O_7, 10H_2O$ ) found naturally in the U.S.A., Chile, Peru, Bolivia, Thibet, California, and elsewhere. Boron is also found in the forms of *boracite* ( $Mg_7Cl_2B_{10}O_{30}$  (Heinz)); *colemanite* or *borate spar* ( $Ca_2B_6O_{11}, 5H_2O$ ), and as *ulexite* ( $Ca_2B_8O_{11}, Na_2B_4O_7, 16H_2O$ ) found in Nevada and California. The composition of some borate minerals, as taken from a pamphlet issued by the Imperial Mineral Resources Bureau, is as follows :

	Colemanite (California)	Ulexite (Chile and Peru)	Boracite (Asia Minor)
Boric acid .. .. .	40.19	44.38	45.89
Lime .. .. .	31.89	16.14	30.62
Magnesia .. .. .	1.50	0.91	0.53
Iron and alumina .. .. .	0.62	0.48	0.98
Soda .. .. .	—	6.50	—
Sodium chloride .. .. .	—	7.46	—
Carbon dioxide .. .. .	8.53	—	—
Sulphur trioxide .. .. .	0.26	3.35	1.25
Water and organic matter .. .. .	5.83	16.25	17.09
Insoluble matter .. .. .	11.18	4.71	3.64
Total .. .. .	100.00	100.18	100.00

Colemanite is of crystal system No. 5, sp. gr. about 2.43. It can be used as a glaze material. Ulexite is amorphous, has a sp. gr. of 1.65. Boracite has a sp. gr. of about 3.

The United States produces approximately 93 per cent. of the world's borates, and Italy and Turkey 2 per cent. each.

In the elemental state boron can be obtained in almost colourless crystals having a density of 2.5, and hardness of 9.5 (Mohs' scale).

There are several methods of preparing this element, one of which consists in heating potassium in the vapour of boron trichloride, thus,  $3K + BCl_3 = 3KCl + B$ ; and another by heating metallic potassium or sodium in admixture with boron trioxide, thus,  $6K + 2B_2O_3 = 3K_2O_2 + 4B$ . It is also obtainable in a pure state by the electrolysis of a fused mixture of potassium carbonate, potassium chloride, and boron trioxide, using a carbon anode and a copper cathode.

When heated strongly in the air, boron burns and combines with both oxygen and nitrogen, forming the oxide and nitride.

Boron is sometimes added to metallic castings, especially those of aluminium and nickel, to strengthen them. When added to steel in minute amount, say 0.002 per cent., boron causes a marked increase in hardenability and other mechanical properties. (See T. G. Harvey, *Iron Age*, 155, 52 (Feb. 15, 1945).)

**Boron Oxide** ( $B_2O_3$ ) is easily heated to fusion as a colourless vitreous solid which becomes opaque by absorption of atmospheric moisture upon allowing to stand after cooling. It has a feeble acidic character, and, when fused with potassium sulphate, potassium borate is produced, while sulphur trioxide is expelled; it is a non-volatile acidic oxide and upon heating liberates volatile acids or their anhydrides from the corresponding salts.

**Boric (Orthoboric) Acid** or **Boracic Acid** ( $H_3BO_3$ ) is found naturally in the water and "soffioni" (steam jets) of volcanic eruptions in Tuscany and elsewhere, and is obtained commercially from such sources. It is a white crystalline body, m.p.  $184^\circ C.$ , very soft and of greasy texture, and soluble in water. It finds many medicinal applications, and is also largely used in glass-making, plating, and metallurgy (as a flux), and as a preservative agent of perishable articles.

At  $100^\circ C.$  boric acid loses water to form **metaboric acid** ( $HBO_2$ ), and this changes at  $140^\circ$  to  $160^\circ C.$  into **tetraboric acid** ( $H_2B_4O_7$ ).

**Sodium Borate (Borax, Borax Glass)**; crystal system No. 5, can be made from boric acid by adding anhydrous sodium carbonate to a boiling solution of the acid, thus,  $4H_3BO_3 + Na_2CO_3 = Na_2B_4O_7 + 6H_2O + CO_2$ . It is chiefly produced from *colemanite* and the Bolivian deposits of calcium borate by boiling the powdered mineral in sodium carbonate solution, thus,  $Ca_2B_6O_{11} + 2Na_2CO_3 = 2CaCO_3 + Na_2B_4O_7 + Na_2B_2O_4$ . By this reaction calcium carbonate is precipitated and the borax can be crystallized out from the solution as  $Na_2B_4O_7 \cdot 10H_2O$ , leaving the sodium metaborate ( $Na_2B_2O_4$ ) in solution, and this is afterwards converted into a further quantity of borax by treatment with carbon dioxide, thus,  $2Na_2B_2O_4 + CO_2 = Na_2CO_3 + Na_2B_4O_7$ .

When crystalline borax is heated, it loses its associated water and passes into a fused glassy mass ("borax glass"), which possesses the power of dissolving many metallic compounds, so that it is used for analytical purposes, the colour which is communicated to the bead of fused material being indicative of the substance under examination. For example, using a looped platinum wire, it can be made to take up a small quantity of borax, which can then be fused so as to make a clear bead in the loop by heating and dipping afresh in the borax,

whilst still hot until it is sufficiently large. If such a bead be touched with a compound of cobalt, it will, upon remelting and subsequent cooling, be found to have an azure or deep blue colour, according to the quantity of cobalt used. Manganese compounds communicate a violet, lilac, or purple colour if the bead be heated in the outer (oxidizing) flame of a blow-pipe; but this colour is lost if the bead be heated in the inner (reducing) flame. Compounds of copper, nickel, iron, chromium, and several other metals yield characteristic colours by this test.

Borax is a valuable flux, and is used as a cleansing agent; in making pottery glazes and enamels; also as a glaze for linen and paper, in tanning, in the manufacture of glue, soap, and glass, and as a food preservative. (See Sodium (Perborate).)

**Boron Trichloride** ( $\text{BCl}_3$ ), produced by heating boron in a current of dry chlorine, is a mobile, colourless liquid, boiling at  $12.5^\circ \text{C.}$ , and is decomposed by water, forming boric and hydrochloric acids.

There are other corresponding halides of boron, namely, **boron fluoride** ( $\text{BF}_3$ ) of b.p.  $-101^\circ \text{C.}$ , **boron bromide** ( $\text{BBr}_3$ ) of b.p.  $90^\circ \text{C.}$ , and **boron iodide** ( $\text{BI}_3$ ) of b.p.  $210^\circ \text{C.}$

**Boron Nitride** (BN) is a white amorphous powder, which, when boiled in caustic alkaline solution, is decomposed with the production of ammonia, thus,  $\text{BN} + 3\text{KOH} = \text{K}_3\text{BO}_3 + \text{NH}_3$ . The nitride is formed by heating boron to a high temperature in nitrogen.

**Boron Triethyl** ( $\text{B}(\text{C}_2\text{H}_5)_3$ ) is a spontaneously inflammable liquid, and the analogous **boron trimethyl** ( $\text{B}(\text{CH}_3)_3$ ) a gas of very unpleasant character, which combines directly with ammonia to form the solid compound  $\text{NH}_3 \cdot \text{B}(\text{CH}_3)_3$ .

**Boron Hydrides**—Several volatile compounds of boron and hydrogen have been described, including  $\text{B}_2\text{H}_6$ ,  $\text{B}_4\text{H}_{10}$ ,  $\text{B}_5\text{H}_9$ ,  $\text{B}_6\text{H}_{10}$ , and  $\text{B}_6\text{H}_{12}$ . Boroethane ( $\text{B}_2\text{H}_6$ ) is probably a resonance molecule.

**BORT** — Crushed diamonds used for lapidary work. (See Carbon.)

**BOYLE'S LAW** — See Gas Laws.

**B.P.L.** — Abbreviation for “bone phosphate of lime,” or calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ).

**BRAIN-MATTER** contains from 80 to 90 per cent. water, the tissue being a mass of colloidal matter of which the envelope is albuminous in character, while the constituent parts are of very complicated constitution, comprising a number of phosphorized substances named variously phosphatides or phospholipins, including lecithin, kephalin, and sphingomyelin, and another group of galactosides or galactolipins, including phrenosin and kersasin.

Lecithin ( $\text{C}_{42}\text{H}_{84}\text{O}_9\text{NP}$ ) upon hydrolysis yields glycerophosphoric acid ( $\text{C}_3\text{H}_9\text{O}_6\text{P}$ ), fatty acids—including palmitic, stearic, and oleic acids—and the base choline ( $\text{C}_5\text{H}_{15}\text{O}_2\text{N}$ ), while kephalin or cephalin is a mixed ester of higher fatty acids, glycerol, phosphoric acid, and colamine.

Sphingomyelin upon hydrolysis yields sphingosine ( $\text{C}_{18}\text{H}_{37}\text{O}_2\text{N}$ ) and choline.

Phrenosin ( $C_{48}H_{93}O_9N$ ) is a dextro-rotatory galactoside and can be separated from sphingomyelin by the use of pyridine as a solvent; upon hydrolysis it yields sphingosine, phrenosinic acid ( $C_{25}H_{50}O_3$ ), and a crystalline sugar named galactose ( $C_6H_{12}O_6$ ).

Kerasin ( $C_{47}H_{91}O_8N$ ) is lævo-rotatory and yields upon hydrolysis the same carbohydrate and lignoceric acid ( $C_{24}H_{48}O_2$ ), accompanied by the base sphingosine.

Cholesterol ( $C_{27}H_{46}OH$ ) constitutes 10 per cent. of the dry brain-matter, and there are also other constituents, including inositol, lactic, and succinic acids, and extractive matters.

It is to the classical researches of Thudichum, Kingzett, and his other assistants that the chemistry of the brain is mainly due, and many important additions to this knowledge have been made in more recent years by Rosenheim, Maclean, and Levene.

(See Reports of the Medical Officer of the Privy Council and Local Government Board, New Series, No. III., 1874, p. 113, and some following ones: Thudichum's *Annals of Chemical Medicine*, vols. i. and ii. (Longmans, Green and Co., London and New York); Thudichum, *A Treatise on the Chemical Constitution of the Brain* (Baillièrre, Tindall and Cox, London); MacLean, *Lecithin and Allied Substances* (Longmans, Green and Co., London); Galactosides, Eggs, and Lecithin.)

**BRANDY** — An alcoholic liquor prepared by distilling fermented wines, and containing about 40 per cent. by volume of ethyl alcohol. Among other ingredients are 0.05 to 0.15 per cent. of higher alcohols, about 0.1 to 0.15 per cent. of esters and about 0.05 to 0.2 per cent. of volatile acid. It is generally coloured with burnt sugar and is used in medicine as well as a beverage.

**BRANNERITE** — See Uranium.

**BRASSES** — Brasses are alloys of copper and zinc, copper preponderating; a prefix is now generally used to indicate any in which a third metal is present, as, for example, tin-brass. "Al-dur-bra" is an aluminium brass. The presence of iron in brass is considered very objectionable. (See Alloys, Bronzes, Copper, and Zinc.)

**BRAUNITE** — See Manganese.

**BRAZILITE (Baddeleyite)** — See Zirconium.

**BRAZIL-NUT OIL** — See Castanha Oil.

**BRAZIL-WOOD DYES** (red and orange), extracted from the wood of the *Cæsalpina crispa* ("Red wood") by boiling water, and used for calico printing and dyeing silk and wool. (See Pernambuco.)

**'BREMEN BLUE'** — Trade name for varieties of specially prepared copper hydroxide or (and) basic copper carbonate. As prepared from copper sulphate solution and sodium hydroxide in certain proportions, it may also contain some basic cupric sulphate ( $CuSO_4 \cdot 3CuO, 4H_2O$ ).

**BREWING** — See Beer.

**BRICKS** are made from clay, from a mixture of clay and sand called *loam*, or from *marl*, which consists of clay and limestone, by moulding and baking. For the inner lining of chemical works-chimneys of an acid-resisting character, vitrified bricks very low in lime content and laid up in acid-proof mortar are used, the mortar being of a nature to resist the particular acid in the smoke stream. They are composed of mixtures of good clay, pure silica sand, kaolin, asbestos fibre, china clay, graphite products, ground gypsum, etc., a common binder being silicate of sodium. Chrome-silica bricks are mechanically stronger at high temperatures than the normal chrome brick, and both have a smaller reversible expansion than silica bricks.

Calcium silicate bricks are made mainly from sand and some 5 to 10 per cent. of slaked lime subjected to heat in an autoclave under pressure of 120 to 180 pounds per square inch by direct steam.

(See *Cement, Concrete, and Bricks*, by A. B. Searle (Constable and Co., London); *Clays, and Refractories*.)

**BRILLIANT GREEN** ( $C_{27}H_{34}O_4N_2S$ )—A water-soluble dye, namely, di-(*p*-diethylamino)-triphenylcarbinol anhydride sulphate, occurring as small lustrous golden crystals; used in medicine as an antiseptic.

**BRIMSTONE**—See Sulphur.

**BRINE (Salt Water)**—Brines are classified principally as chloride, sulphate, carbonate, and mixed waters, and also of less importance as siliceous, nitrate, phosphate, borate, and acid waters. Many typical analyses are compiled by F. W. Clarke in *The Data of Geochemistry* (U.S. Geological Survey Bulletin). Some analyses are presented in the following table:

Brine	Cl	Br	SO <sub>4</sub>	CO <sub>3</sub>	Na	K	Ca	Mg	SiO <sub>2</sub>
Syracuse, New York	58.85	0.01	2.29	0.01	37.29	0.03	1.28	0.23	
Hutchinson, Kansas	59.60		1.33		38.38		0.55	0.11	0.03
Vichy, France ..	6.17		3.75	45.57	35.27	2.88	2.29	1.11	1.32
Wiesbaden, Ger- many .. ..	56.58	0.04	0.78	3.13	32.60	1.16	4.05	0.61	0.76
Harrogate, England	58.81	0.19		2.12	33.61	0.48	2.65	1.37	0.07
Cheltenham, Eng- land .. ..	6.56		57.42	6.48	13.51	0.48	8.33	7.03	0.16
Mittagong, New South Wales ..	27.34			30.58	7.13	8.96	4.25	5.89	Fe15.85

See *Industrial Development of Searles Lake Brines*, by J. E. Teeple (Reinhold Publishing Corp., New York); and *Water (Sea Water)*.

**BRINELL BALL TEST** for hardness of metals. The measured determination of indentation on prepared surfaces caused by applied heavy weight or blow of steel ball. The Brinell hardness test is applied to small test samples having a flat face, carefully polished to receive the impression from a hard steel ball, which is thrust against the surface by a heavy load steadily applied. The diameter of indentation produced must be measured under a microscope, or by means of a graduated V-scale. Portable apparatus for these tests is obtainable, the ball

indentation being caused by a hammer blow, which simultaneously indents a bar of known hardness. The hardness of the material being tested is then determined by reference to a table of data furnished with the apparatus.

#### TYPICAL BRINELL HARDNESS VALUES

Admiralty bronze .. .. .	75
Copper .. .. .	90
Phosphor bronze .. .. .	100-130
Mild steel .. .. .	115-150
Cast iron, soft .. .. .	150
Cast iron, hard .. .. .	170
Steel castings, soft .. .. .	100-150
Steel castings, hard .. .. .	165-205
Steel, Bessemer .. .. .	185
Steel rails .. .. .	190-205
Carbon steel, rolled .. .. .	225-275
Carbon steel, toughened .. .. .	330-345
Manganese steel forging .. .. .	275
Manganese steel, toughened .. .. .	205-230
Nickel-chromium steel, hardened .. .. .	420-720
Tungsten steel, self hardening .. .. .	625
High-carbon steel, hardened .. .. .	640-710
Gauge steel, hardened .. .. .	675-750

**BRIQUETTING** — The process of forming powdered, granular or fibrous materials into blocks by mechanical pressure in a mould, usually after the addition of a binder. Briquetting is most commonly applied to coal and anthracite fines, the standard binders being coal-tar pitch and petroleum pitch or cracked asphalt. The coal, mixed with 7-10 per cent. of binder, is heated by superheated steam and fed to mechanical presses. These are of two types, roller presses for the small egg-shaped briquettes or "ovoids" used domestically, and plunger presses making the larger rectangular briquettes for burning under industrial and locomotive boilers. The following are typical British specifications for briquetting binders:

#### *Coal Tar Pitch*

Ash .. .. .	less than 1 per cent.
Volatile matter .. .. .	55/60 per cent.
Softening point .. .. .	54/55° C.
Melting point .. .. .	70/80° C.
Free carbon .. .. .	less than 20 per cent.

#### *Petroleum Pitch*

Specific gravity at 60° F. .. .. .	1.127
Flash-point (open cup) .. .. .	597° F.
Penetration at 77° F. (100 g./5 sec.) .. .. .	0/1cm.
Penetration at 114° F. (50 g./5 sec.) .. .. .	8/9cm.
Softening point (R. and B.) .. .. .	180/200° F.
Solubility in CS <sub>2</sub> .. .. .	99.5 per cent.

**BRITANNIA METAL** — Used for making domestic table-ware, such as spoons, cans, teapots, etc. Its composition is given under the heading of Alloys, and occasionally 2 or 3 per cent. zinc is incorporated. (See Alloys, Antimony, and Tin.)

**BRITISH GUM** — See Starch.

**BROMETHOL** ("Avertin") — A solution of tribromoethyl alcohol in amylene hydrate, containing 1 gram in 1 millilitre; used in medicine as a general anæsthetic. (See Tribromoethyl Alcohol.)

**BROMINATION** — The chemical introduction of bromine into the constitution of a substance, commonly an organic substance, for example, the action of bromine on benzene whereby bromobenzene ( $C_6H_5Br$ ) and hydrobromic acid ( $HBr$ ) gas are simultaneously formed.

**BROMINE** ( $Br$ ) and its Compounds — Atomic weight, 79.916. See Elements for other data. Bromine is found in sea-water in combination with potassium, sodium, and magnesium—about 66 to 70 parts per million—and more abundantly in certain mineral waters and salt springs. The Stassfurt *carnallite* deposits contain it (combined with magnesium), and from this salt it is made, while other supplies are afforded by the Dead Sea water, the electrolysis of residual waste brine of the salt industry, and on a large scale from sea-water by the action of chlorine at Cape Fear, North Carolina, which process is described by L. C. Stewart in *Ind. Eng. Chem.*, 26, 361 (1934).

Bromine is a heavy, mobile liquid of a red-brown colour and strong, unpleasant smell; gives off vapour of the same colour when exposed to the air, solidifies at  $-7^\circ C.$  to a crystalline mass, has boiling point of  $59^\circ C.$ , but gives off copious vapours at room temperature, is very poisonous, has a strong corrosive action on the skin, and is soluble in water, alcohol, and ether. It is used in the dye industry, in organic synthesis, the production of bromides, and ethyl bromide (for production of tetraethyl lead).

The soluble salts, sodium bromide ( $NaBr$ ), potassium bromide ( $KBr$ ), and ammonium bromide ( $NH_4Br$ ), are all used in the preparation of certain medicinal sedative mixtures.

**Hydrobromic Acid** or **Hydrogen Bromide** ( $HBr$ ) (corresponding to hydrochloric acid) is produced when a mixture of hydrogen and bromine vapour is burned or passed over a spiral wire of platinum maintained at a bright red heat; or by dropping bromine upon wetted red phosphorus, which results in the formation of phosphorous acid ( $H_3PO_3$ ) and evolution of hydrobromic acid. It is best prepared by interaction of bromine and sulphur dioxide, and recovery by distillation. It is a colourless gas of pungent odour, which fumes in the air and is very soluble in water, the aqueous solution resembling one of hydrochloric acid in its general chemical behaviour.

**Bromic Acid** ( $HBrO_3$ ) is only known in solution, and it forms bromates analogous to the chlorates, by corresponding reactions, potassium bromate having the formula  $KBrO_3$ .

**Bromine Trifluoride** ( $\text{BrF}_3$ ) of b.p.  $135^\circ \text{C.}$ , and **bromine iodide** ( $\text{BrI}$ ) of sublimation temperature about  $42^\circ \text{C.}$  and sp. gr. 4.4 are known.

**Bromine Hydrate** ( $\text{Br}_2 \cdot 10\text{H}_2\text{O}$ ). Decomposes at  $7^\circ \text{C.}$

**BROMOFORM** ( $\text{CHBr}_3$ )—A colourless heavy liquid; sp. gr. 2.890 and b.p.  $150.4^\circ \text{C.}$  (corresponding to chloroform and iodoform), made by distillation from a heated mixture of ethyl alcohol, bromine, and sodium hydroxide; soluble in alcohol and ether, and used in medicine. It is decomposed by light, but may be preserved by the addition of a small amount of ethyl alcohol.

**BROMONAPHTHALENE (Alpha)** ( $\text{C}_{10}\text{H}_7\text{Br(I)}$ )—A yellow liquid, miscible with alcohol, ether, and benzene; made by the bromination of naphthalene, the alpha substitution product being the only mono bromination derivative obtained thereby. It melts at  $5^\circ$ , boils at  $281^\circ \text{C.}$ , and is used in organic synthesis.

**BROMVALETONE**—A white crystalline solid, namely, 2-monobromo-*isovalerylurea*; slightly soluble in water, soluble in alcohol and in ether; m.p.  $145^\circ$  to  $153^\circ \text{C.}$  Used in medicine as a rapidly acting hypnotic.

**BROMYRITE (Bronite)**—Natural silver bromide ( $\text{AgBr}$ ), of sp. gr. 5.8 to 6, and crystal system No. 1, containing 57 per cent. of silver, found in New Mexico and Nevada.

**BRONZE BLUES**—Forms of Prussian blue.

**BRONZE POWDERS**—Used for japanning and other decorative applications, and made of many shades; compounded of alloys of various metals—copper, zinc, iron, tin, lead, vanadium, etc.—beaten into leaf and reduced to powder, with or without admixture with other compounds, according to the desired colour and properties. Oxygen in the copper is an undesirable impurity as concerns bronze powders.

**BRONZES**—Bronzes are generally considered as alloys of copper and tin with numerous modifications. By one classification, "bronzes" consist of copper and aluminium only, good bronze containing from 3 to 5 per cent. copper. So-called "steel bronze" contains 8.5 per cent. copper and a proportion of silicon, while "acid bronze" contains about 10 per cent. copper. Bronze M.A. is a standardized non-ferrous alloy prepared to meet the need of a gun-metal and a phosphor bronze, the analysis being as follows: Copper, 85.5 per cent.; tin, 9.96 per cent.; zinc, 1.86 per cent.; lead, 1.83 per cent.; phosphorus, 0.25 per cent.; antimony, 0.24 per cent.; iron, 0.07 per cent.; nickel, 0.04 per cent.; and arsenic, 0.06 per cent. Without corresponding to any particular specification, it is said to contain all the elements usually met with in ordinary gun-metal and bronzes. (See *The Metallurgy of Bronze*, by H. C. Dews (Sir Isaac Pitman and Sons, London); Alcobronze, Alloys, Aluminium Bronzes, "Coronium," Phosphor Bronze, and Tin.)

**BROOKITE** ( $\text{TiO}_2$ )—A titanium mineral of crystal system No. 4, and sp. gr. 3.8 to 4.2. (See Titanium.)

**BROTEX**—A hybrid biennial plant of recent origin described as of rapid growth, producing fibre for textiles, cellulose for paper-making, and seed for cattle-cake, having an oil content of 15 per cent. and belonging to the order *Malvaceæ*. (See *Empire Forestry Journal*, vol. 8, No. 1.)

**BROWN COALS** — These, like lignites, are differentiated from the geologically older bituminous coals, inasmuch as (1) in the raw state they contain much more water (varying from 20 to 50 per cent.) ; (2) by air-drying they usually disintegrate more or less ; (3) they are naturally devoid of coking properties ; (4) in the dry, ashless state they usually contain more than 75 per cent. carbon and 20 per cent. oxygen ; and (5) when carbonized at 900° C. they yield upwards of 45 per cent. volatile matter. The coke is of about 0.5 sp. gr. They lend themselves better to the process of "berginization" than the better known harder varieties of coals. The more recent brown coals have an amorphous earthy character, while the older varieties exhibit either a laminated structure or a well-marked conchoidal fracture. Brown coals do not give such high yields of tar and oils as bituminous coals. In the province of Alberta (Canada) there are large deposits of brown coal. (See Coal, Lignite, and Peat.)

**BROWNIAN MOVEMENT** — See Colloid Chemistry.

**BRUCINE** — See Nux Vomica.

**BRUCITE** ( $\text{MgO}, \text{H}_2\text{O}$ ) — A mineral of crystal system No. 3, and sp. gr. 2.35. (See Magnesium.)

**BRUNSWICK BLACK** is prepared by melting together bitumen and boiled linseed oil in the proportions of 2 to 1, and adding two parts of turpentine to the mixture upon cooling.

**BRUNSWICK GREEN** — A trade name used in respect of several mixtures of Prussian blue and chrome yellow with or without other loadings, more properly applied to copper oxychloride. (See Copper Compounds.)

**BRUSHITE** — A natural hydrated calcium phosphate ( $\text{CaHPO}_4, 2\text{H}_2\text{O}$ ) found in the guano of Aves Island and Sombbrero.

**B.S.I.** — British Standards Institution, a body which issues standards and specifications of many materials related to chemistry.

**B.Th.U. (B.T.U.)** — British Thermal Units. (See Heat.)

**Bu** — A symbol used for butyl ( $\text{C}_4\text{H}_9$ ) radical.

**BUCKWHEAT** (*Fagopyrum esculentum*) is grown in the Volga basin, Caspian Sea area, parts of Central Asia and the United States. It is used for flour, groats, and middlings.

**BUFFER ACTION** — See Hydrogen-Ion Concentration, and Volumetric Analysis.

**BURETTE** — A graduated glass tube, open at the top and drawn out below, where it is fitted either with a glass stop-cock, or rubber tubing and a pinch-cock, for delivering measured quantities of liquids. (See Volumetric Analysis.)

A gas burette is designed with a stopcock at the top of the container for incoming and outgoing gas, and with a tubular opening at the bottom for liquid connecting to a levelling tube, which is used for forcing the gas sample in and out at the top of the burette.

**BURGUNDY PITCH** — A resinous substance obtained from the stem of *Picea excelsa*, purified by melting under water and straining. It consists of a hard, yellowish-brown plastic solid, having an aromatic odour ; soluble in hot alcohol and formerly used in medicine in the preparation of plasters. A factitious Burgundy Pitch is prepared by mixing common pitch with colophony and turpentine and agitating the mixture with water.

**BURNERS** — Gas-burners are of various types, according to the application that is to be made of them, apart from those used for illumination.

**Fish-Tail Burner** — A burner with a flame like a fish-tail or bat's wing in general form, and is chiefly used in the bending of glass tubes. The luminosity of the flame is due to the imperfect combustion of the gas, and consequent production of minute particles of the carbon constituent in an incandescent form.

**Bunsen Burner** — This consists of an iron or brass tube fixed to a foot-stand, and fitted with a mechanical arrangement below, whereby air can be admitted in regulated amount into admixture with the gas before burning. The gas issues from a small jet set inside at the base of the tube, and the air is admitted through several small holes in the surrounding tube also situated near its base, the amount of air being regulated by a movable cylinder of metal capable of closing these openings more or less as desired. In practice there is used about 1 volume of gas to  $2\frac{1}{2}$  volumes of air. By this admixture the heat is intensified, perfect combustion of the carbon of the gas, as also of the hydrogen, being secured, thus producing a practically smokeless blue flame. Such burners are often provided with a movable ring which fits on to the top of the burner tube, so that, when desired, the flame may be broken up and caused to assume a rose or ring form made up of a number of small blue flames, instead of the one long vertical column of flame. Both of these forms are employed for heating liquids contained in flasks or beakers, or for heating solid substances contained in crucibles, dishes, etc. ; also for applying heat to sand-baths, water-baths, and water-ovens.

The flame of a Bunsen burner (like all ordinary flames) consists of two cones — the inner one, in which heated but imperfectly burned gases exist ; and the outer one, where oxygen is in excess on the outside edge. Upon holding a bright copper wire across the flame so as to bisect the inner one, the wire will become coated with black copper oxide at the outer edges, while that part in the centre will remain bright. If now the blackened part be placed in the inner cone, the oxide will be reduced again to the metallic state, parting with its oxygen constituent to the gases in course of combustion. The outer area is consequently called the *oxidizing flame*, and the inner cone the *reducing flame*.

**Meker Burner** — The fuel gas and air are mixed as in a Bunsen burner, but more effectively in a larger, expanded-upward, mixing head, and the mixture emerges at the top through numerous openings. The blue cones are many and small, and the result is a very high flame temperature of over  $2,000^{\circ}\text{C}$ . Several modifications of this burner are marketed.

When coal gas is burned in a current of air, water and carbon dioxide are the products of its combustion. (See Flame.)

**Burners** for sulphur-containing ores and similar materials are of the horizontal, rotating kiln type and of the vertical tray type with rotating rake arms.

**BURNT ALUM** — See Aluminium (Alums).

**BURNT LIME** — See Calcium (Lime).

**BUTACAINE SULPHATE** ("Butyn")  $((C_{18}H_{30}O_2N_2)_2 \cdot H_2SO_4)$  — A white, crystalline compound, being the sulphate of  $\gamma$ -di-*n*-butylaminopropyl-*p*-aminobenzoate; soluble in water, alcohol, and acetone; slightly soluble in chloroform; insoluble in ether; m.p.  $100^\circ$  to  $103^\circ$  C. Used in medicine instead of cocaine.

**"BUTACITE"** (Du Pont) — Trade-mark for polyvinyl acetal synthetic resin. Used specially as interlayer for safety glass.

**BUTADIENE** ( $C_4H_6$ ) — There are two isomeric forms, namely, 1,2- of formula  $CH_3 \cdot CH : C \cdot CH_2$ , b.p.  $10.3^\circ$  C., sp. gr. 0.65, and 1,3- of formula  $CH_2 : CH \cdot CH : CH_2$ , b.p.  $-4.4^\circ$  C., sp. gr. 0.62. The latter form, the one that has attained great importance in the synthesis of rubber, was made, during World War II, in the U.S.A. principally from ethyl alcohol, and in Germany from acetylene via acetaldehyde, acetaldo, and 1,3-butanediol, and from acetylene plus formaldehyde via  $H_2C(OH) - C : C - (HO)CH_2$  and 1,4-butanediol; later methods in the U.S.A. use petroleum either by direct cracking or by the catalytic dehydrogenation of butene. (See *Newer Methods of Preparative Organic Chemistry* (Interscience Publishers, New York), and "Conversion of 2,3-Butylene Glycol to 1,3-Butadiene, by Pyrolysis of Diacetate," by S. A. Morell and others (*Ind. Eng. Chem.*, **37**, 877 (1945)).)

**BUTANE** — See Hydrocarbons.

**BUTANOL** (Butyl Alcohol) — See Acetone, and Alcohols.

**BUTEA GUM** (Bengal Kino) — The hardened juice from incision made in the stems of *Butea frondosa* (India and Burma). It is soluble in water when fresh, but rapidly oxidizes and becomes insoluble; used as a tanning material.

**"BUTESIN"** — See Butyl Aminobenzoate.

**BUTOBARBITONE** ("Soneryl") — A white crystalline solid, namely, 5-*n*-butyl-5-ethylbarbituric acid; slightly soluble in water, soluble in alcohol and in solutions of alkaline hydroxides. Used in medicine as an hypnotic and sedative.

**"BUTOLAN"** — See Diphenan.

**BUTTER** — The fat of milk separated by churning. In addition to butter fat, butter from cow's milk contains vitamin A, water, and

protein (curd). The composition of butter varies widely, but the analysis of a typical sample is as follows :

	Per Cent.
Fat .. .. .	86.85
Curd .. .. .	0.59
Salt .. .. .	1.02
Water .. .. .	11.54
	<hr/> 100.00

One published analysis of the fats of *dry* butter is as follows : palmitin, myristin, and other hard fats 53.98 per cent., olein 37.82 per cent., butyrin and other constituents 8.20 per cent. When hydrolysed, butter yields, according to one account, as follows : palmitic acid, 18.23 per cent. ; myristic acid, 11.08 per cent. ; lauric acid, 16.40 per cent. ; stearic acid, 0.49 per cent. ; oleic acid, 36.10 per cent. ; caproic, caprylic, and capric acids, 3.23 per cent. ; butyric acid, 6.13 per cent. ; glycerine, 12.50 per cent. According to C. Ainsworth Mitchell, the stearic acid content of butter fat ranges from nil up to 22 per cent.

Butter has sp. gr. of 0.926 to 0.940 ; sap. v. of 220 to 233 ; i.v. of 26 to 38 ; and ref. ind. of 1.4650 at 60° C. The fat of goat's butter gives figures ranging as follows : Reichert-Wollny value 20.8 to 27.77, ref. ind. 1.4541 to 1.4559, i.v. 24.73 to 34.84, and sp. gr. at 100° F. from 0.9169 to 0.9346.

In early chemistry, butter of antimony was anhydrous antimony trichloride, and butter of zinc similarly anhydrous zinc chloride.

**BUTYL** — The univalent radical— $C_4H_9$ .

**BUTYL ACETATE** ( $CH_3.CO\ddot{O}.C_4H_9$ ) is made from butyl alcohol, has sp. gr. 0.882, b.p. 126.5 (normal ester), and is used largely as a solvent in making pyroxylin, lacquers, and perfumes.

**BUTYL ALCOHOL** — See Acetone, and Alcohols.

**BUTYL AMINO BENZOATE** ("Butesin," "Scuroform") ( $C_{11}H_{15}O_2N$ ) — A white, crystalline compound, namely, *n*-butyl-*p*-aminobenzoate ; slightly soluble in water ; soluble in alcohol, chloroform, and ether ; m.p. 57° to 59° C. Used in medicine as a local anæsthetic.

**BUTYL ETHERS** — See Ethers. Several are listed under Monobutyl Ether of each.

**BUTYLAMINE** — See Amines.

**BUTYLENE** — A hydrocarbon of the olefin series. (See Hydrocarbons.)

"**BUTYN**" — See Butacaine Sulphate.

**BUTYRIC ACID** ( $CH_3(CH_2)_2COOH$ ) is produced by the oxidation of the corresponding butyl alcohol and in the butyric fermentation of sugar or starch, being secondarily produced from lactic acid ; it also occurs in glyceric combination in butter, and communicates the so-called rancid odour to that substance when stale. It is also produced by the "Ketol" process in France, calcium butyrate and cellulose butyrate being among the products, the last named being a substitute for cellulose acetate in making "Rayon." It is found present in the

free state in perspiration and in the secretions of certain insects. It is a colourless liquid of rancid odour when volatilized, b.p.  $164^{\circ}\text{C.}$ , sp. gr. 0.964; is used in medicine, varnish-making, and to some extent in tanning processes. (See Acids.)

**BUTYROMETER** — An instrument for determining the amount of butter in milk.

**Bz** — A symbol used for benzoyl ( $\text{C}_6\text{H}_5\text{CO}$ ) radical.

**CACAO (Cocoa, Theobroma Seed)** — The fermented and dried seeds of *Theobroma cacao* and other plants belonging to the *Sterculiaceæ* of Africa, South America, West Indies, and certain tropical parts of Asia.

The beans, which differ in certain particulars, all contain much fatty matter, and about 1 per cent. of theobromine ( $\text{C}_7\text{H}_8\text{O}_2\text{N}_4$ ), or from 2.2 to 3.9 per cent. calculated on the dry fat-free material, together with about 0.4 per cent. of caffeine. The theobromine content of the nib of the bean varies with the degree of fermentation to which the latter has been subjected, and also with the variety—Criollo (whitish bean) or Forastero (purple bean)—to which it belongs, the Forastero being the richer in content. The shells themselves contain approximately 0.2 per cent. of theobromine, passing thereinto during fermentation. The germ, as commercially separated from roasted cacao beans, contains about 2.1 per cent. theobromine. The aroma of cacao is due to the presence of about 0.006 per cent. of linaloöl. The fat ranges from 50 to 56 per cent., has the consistence of suet, and is a mixture of the glycerides of oleic, stearic, and palmitic acids, with some proportion of lauric acid. An analysis gives the proportions of acids as follows: oleic, 43 to 45 per cent.; palmitic, 23 to 25 per cent.; and stearic, 31 to 33 per cent.

Cacao shell is used to some extent as an ingredient in compounding cattle foods, also as a fuel, and as a manure after disintegration.

Chocolate is a preparation of roasted cacao beans with flour or other farinaceous matter and sugar; whereas cacao is the powder made from the roasted beans. (See *Cocoa and Chocolate: their Chemistry and Manufacture*, by R. Whympers (J. and A. Churchill, London); *Cocoa and Chocolate Manufacture*, by H. W. Bywaters (J. and A. Churchill, London); *Cocoa: World Production and Trade* (H.M. Stationery Office); and Theobromine.)

**CACAO BUTTER (Cocoa Butter, Oil of Theobroma)** — The solid fat obtained by expression from the roasted and crushed cacao beans. It consists of a mixture of glycerides (see Cacao).

Cacao butter is of sp. gr. 0.95 to 0.97; m.p., from  $32^{\circ}$  to  $34^{\circ}\text{C.}$ ; iodine value, from 35 to 38; saponification value, 192 to 198, and refractive index of  $45.6^{\circ}$  to  $46.5^{\circ}$  (butyro-refractometer at  $40^{\circ}\text{C.}$ ). It is used in making cosmetics, in pharmacy, and in chocolate making. Cacao butter is quite distinct from coconut oil, which is yielded by the cocoa palm, *Cocos nucifera*.

The fat resulting from the fermentation of cacao shell (up to 4 per cent.), after refining, can be used for edible purposes and is also suitable for soap-manufacture.

**CACODYL** — A methyl arsenide ( $\text{As}_2(\text{CH}_3)_4$ ) prepared by heating a mixture of arsenious oxide and potassium acetate. It is a colourless liquid, insoluble in water, of offensive garlic-like odour, b.p.  $170^\circ \text{C}$ ., extremely poisonous, and readily inflammable in air. It combines with chlorine, and acts as an organo-metallic radical, forming, for example, cacodylic acid ( $(\text{CH}_3)_2\text{AsO}\cdot\text{OH}$ ), a colourless, odourless, poisonous, crystalline body, soluble in water and alcohol. The use of these aliphatic arsenicals in medicine has been discontinued because of their toxicity.

**CADAVERINE** — See Albumins, and Ptomaines.

**CADE OIL (Juniper Tar Oil)** — Obtained by the dry distillation of the wood of the *Juniperus oxycedrus* (Mediterranean countries). A thick, clear liquid of burning, bitter taste, sp. gr. 0.98 to 1.06 at  $15^\circ \text{C}$ .; soluble in alcohol and ether; used in perfumery, medicine, and for making animal soap, etc. It contains guaiacol and cadinene.

**CADINENE** ( $\text{C}_{15}\text{H}_{24}$ ) — A lævorotatory, dicyclic sesquiterpene, occurring in cade, betel, camphor, juniper, patchouli, and olibanum oils. It is a viscous liquid of sp. gr. about 0.92, b.p.  $274^\circ \text{C}$ ., and forms beautiful additive compounds with the halogen acids.

**CADMIUM (Cd) and its Compounds** — Atomic weight, 112.41. See Elements for other data. Cadmium is found naturally in the form of sulphide in a rare mineral named *greenockite* (crystal system No. 3, and sp. gr. 4.8), and in a number of zinc ores, both as sulphide and carbonate, but not in the metallic state. It is produced in the process of extracting zinc from its ores, being found in the first fractions coming over when distilling them, partly in the metallic condition and partly as oxide, the proportion being about 1 part cadmium to 200 parts zinc. It can also be recovered from the "bag-house" condensation products from lead and copper furnaces by an electrolytic process.

Cadmium is of a bluish-white colour, and an interesting property is its power of lowering the melting-point of certain alloys when incorporated in small proportion, thus making it useful in the manufacture of fusible plugs in sprinkler systems for fire prevention. One alloy in particular, composed of 90.8 parts lead, 7.8 parts cadmium, and 1.4 parts zinc, is an excellent one for general soldering purposes involving the use of the iron. Cadmium also gives valuable protection to iron and steel against atmospheric corrosion when electrolytically deposited thereon as a coating, and is not so readily corroded as zinc, hence the occasional practice of adding about 5 per cent. of cadmium powder to the zinc dust used in "sherardizing." (See C. L. Wilson and O. J. Wick, on "Cadmium-Indium Alloy System" (*Ind. Eng. Chem.*, 29, 1164 (1937).)

The compounds include the **oxide** ( $\text{CdO}$ ), which is formed when the metal is burned in the air; the **hydroxide**  $\text{Cd}(\text{OH})_2$ , a white compound insoluble in water but soluble in acids and ammonium hydroxide; the **chloride** ( $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ ), a soluble salt used in photography, dyeing, plating practice (in place of zinc), and calico-printing; the

CADMIUM METAL, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country	Cadmium Metal Metric Tons			
Germany .. .. .	..	..	..	400
Belgium .. .. .	..	..	..	330
Norway .. .. .	..	..	..	170
Poland .. .. .	..	..	..	150
Italy .. .. .	..	..	..	140
United Kingdom .. .. .	..	..	..	120
France .. .. .	..	..	..	110
				—————
				1,420
U.S.S.R. .. .. .	..	..	..	50
U.S.A. .. .. .	..	..	..	1,790
Mexico .. .. .	..	..	..	730
Canada .. .. .	..	..	..	360
				—————
				2,880
South-West Africa .. .. .	..	..	..	170
Australia .. .. .	..	..	..	200
Sum of above .. .. .	..	..	..	4,720

WORLD PRODUCTION, approximately the above.

**selenate** ( $\text{CdSeO}_4 \cdot 2\text{H}_2\text{O}$ ); the **selenide** ( $\text{CdSe}$ ) used as a pigment in rubber; the **bromide** ( $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ ), a yellow, soluble, crystalline salt, used in photography; the **sulphide** ( $\text{CdS}$ ), a yellow compound, insoluble in water, used as a pigment in oil and water-colour painting; the **nitrate** ( $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ), a white salt, soluble in water, used for colouring glass and porcelain; and **tungstate** ( $\text{CdWO}_4$ ), a yellow crystalline salt, soluble in alcohol, and used in making fluorescent paint.

Red cadmium pigments ranging from orange to purplish-red are made by mixing cadmium sulphide with cadmium selenide and barium sulphate. Pale cadmium colours are produced industrially by adding ammonium monosulphide to cadmium oxalate, observing certain conditions of dilution and temperature, and dark colours from sodium monosulphide and cadmium carbonate, the nitrate being used as the source of the other cadmium compounds.

**Cadmium oleate** exhibits greater resistance to hydrolysis than zinc oleate and promises to have a superior industrial future than the zinc compound as an impregnating material. Trials have shown it to be very effective in waterproofing textiles and for impregnating porous ceramic articles.

“**CADMOPONES**” (**Cadmium Lithopones**) — See Paints.

**CÆSIUM** — See Cesium.

**CAFFEINE (Theine)** ( $C_8H_{10}O_2N_4, H_2O$ ). — A purine alkaloid (1,3,7-trimethyl-2,6-dihoxypurine), being the active principle of coffee (which contains varying proportions up to about 2 per cent.), kola nuts, tea (which contains from 2.5 to nearly 5 per cent.), and the *Yucca* plant. When anhydrous it melts at  $235^\circ C.$ , the hydrate sublimates at  $180^\circ C.$ , and crystallizes from water in white silky needles, having a slightly bitter taste; soluble in chloroform, in alcohol, and in solutions of sodium benzoate and sodium salicylate. Caffeine stimulates the higher centres of the brain, increases the activity of muscle, and has a diuretic effect. It is used in medicine as a stimulant. (See Coffee, Purine, and Tea.)

**CAJUPUT (Caseput), OIL OF** — An essential oil used in medicine, obtained in India and the Molucca Islands, by distillation with water of the leaves of the *Melaleuca leucodendron* (N.O. Myrtaceæ). It is of green colour and camphoraceous odour, soluble in alcohol and ether, contains cineol — at times up to 58 per cent. or more — terpineol, etc. Sp. gr. 0.92 to 0.93 at  $15^\circ C.$ ; opt. rot.  $-0^\circ$  to  $-4^\circ$ ; ref. ind. 1.460 to 1.470 at  $25^\circ C.$

**CALABAR BEAN (Ordeal Bean)** — The ripe seeds of *Physostigma venenosum*, a woody climbing plant indigenous to West Africa. It contains from 0.05 to 0.3 per cent. of total alkaloids, the most important of which is physostigmine (eserine). (See Physostigmine.)

**CALAMINE (Smithsonite)** — Mineral zinc carbonate ( $ZnCO_3$ ), of crystal system No. 3, and sp. gr. 4 to 4.5. (See Zinc.)

**CALAMUS OIL (Oil of Sweet Flag)** — Distilled from the rhizome of *Acorus calamus*, and used in perfumery, etc. It is a thick, yellowish, aromatic oil, soluble in alcohol and ether, of sp. gr. about 0.96, and ref. ind. about 1.5; yield is 2.8 per cent.

**CALANDRIA** — The steam chest of an evaporator. It generally consists of a short cylindrical shell containing a nest of tubes expanded into tube-plates at both ends. The liquid to be evaporated circulates through the tubes, while steam is admitted to the space between the tubes and the shell. (See Evaporation.)

**CALCAREOUS SPAR** — Native crystallized calcium carbonate.

**CALCINATION** — Burning (calcining) or incinerating operation employed for the conversion of chalk into lime by burning; the reduction of sulphur content of certain iron ores; the dehydration of fuller's earth and bauxite; the preparation of barium sulphide and lithopone; the revivification of bone black; the calcination of lime sludge, bones, and similar operations. Such operations are carried out in the laboratory for the most part in crucibles, and in manufacturing operations in rotary kilns and reverberatory furnaces. (See Calx, Kilns, Ores, and Oxidation.)

When conducted in the air it is a process of oxidation largely resorted to, as a stage in the separation of metals from their ores.

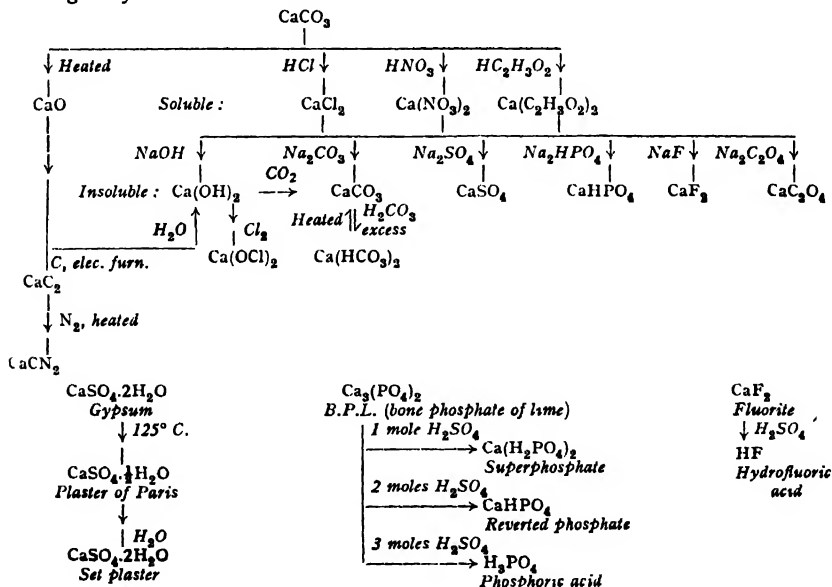
**CALCIFEROL** — See Vitamins (Vitamin D).

**CALCITE** ( $CaCO_3$ ) — See Calcium.

Calcium is a soft and whitish metal obtained in the metallic state by the electrolysis of fused calcium chloride using a carbon anode, and in crystalline form by condensation of its vapour. It is a good reducing agent, and when heated in oxygen to 300° C. it inflames, and the lime thus produced is fused by the heat. Calcium is added in small percentage to various metals and alloys to augment their mechanical properties (see *Calcium, Metallurgy and Technology*, by C. L. Mantell and C. Hardy (Reinhold Publishing Corp., New York)). Examples of this use are "Frery Metal" and magnesium-calcium alloy.

### CHARTS SHOWING PRINCIPAL INTER-RELATIONSHIPS

Arranged by the Editor.



**Lime (calcium oxide, burnt lime)** ( $\text{CaO}$ ) is made on a very large scale by burning limestone (chalk) with coal in kilns lined with basic bricks containing 50 per cent. silica, when the carbonate parts with carbon dioxide and leaves lime (quicklime) behind; or the limestone is baked alone in furnaces at a heat sufficiently great to break it up into quicklime and carbon dioxide gas, thus, ( $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$ ).

Rotary kilns present certain advantages over shaft kilns, and a minimum temperature of  $900^\circ \text{C.}$  is required, the regulation of the air supply being the most important factor in determining the efficiency and fuel economy. It is estimated that 4 tons of lime should be obtained per ton of fuel burned, with a thermal efficiency of over 60 per cent. When produced at  $1,200^\circ \text{C.}$  lime is "overburned," and does not slake so readily as that resulting from production at  $1,100^\circ \text{C.}$ , and when burned at  $1,700^\circ \text{C.}$ , it is much overburned, and slakes very slowly.

Quicklime is a white and difficultly fusible substance which, when mixed with water, forms the white powder known as **calcium hydroxide**, or slaked lime,  $\text{Ca(OH)}_2$ , which in the pure state is said to have a density of 2.24. Slaking with excess water produces a product much finer than that which results from use of the theoretical quantity of steam. During slaking with a minimum of water the heat evolved rises above  $270^\circ \text{C.}$ , a temperature at which untreated and dry woods will commence to burn. "Hydralime" is a brand described as a practically pure hydroxide, while another grey variety contains proportions of silica and alumina, said to endow the material with special setting property and strength.

Lime (the oxide or hydroxide) is used very largely in the making of glass, mortar, putty, and cement; as an accelerator in the rubber industry; the preparation of limewash, distemper paints, and as the base in the manufacture of bleaching-powder; also as a dressing for skins to remove grease and fur, and for application to clayey soils to make the land more friable. Lime constitutes an important plant factor, capable as it is of acting chemically, physically, and bacteriologically in the soil; it can also be employed as a fungicide, insecticide, and water softener.

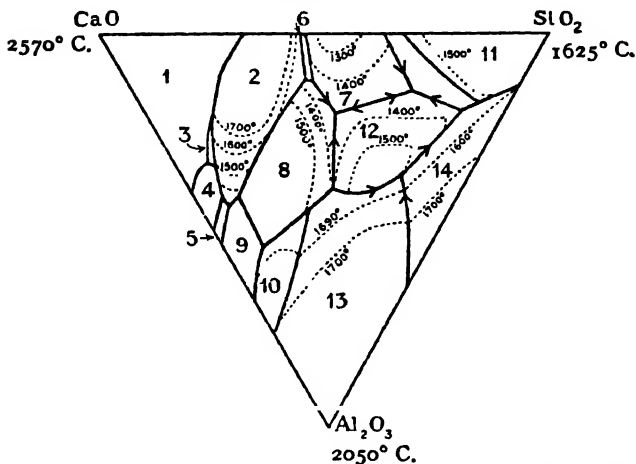
**Lime-Water** is a solution of calcium hydroxide ( $\text{Ca(OH)}_2$ ), which is soluble in water to the extent of 0.14 part in 100 parts at the ordinary temperature, or about 121.7 grains per gallon.

**Calcium Carbonate** ( $\text{CaCO}_3$ ) occurs in nature in a great variety of forms, both anhydrous and hydrated, the latter as *hydrocalcite* ( $\text{CaCO}_3 \cdot 5\text{H}_2\text{O}$ ) and as  $\text{CaCO}_3 \cdot 3\text{H}_2\text{O}$ . A hexahydrate ( $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$ ) is also known. Calcium carbonate is almost insoluble in water, but dissolves readily when the water contains carbon dioxide, and the so-called *temporary hardness* of water is due to the amount thus held in solution, but which is deposited when the water is boiled owing to the consequent expulsion of that gas. The *permanent hardness* of water is due principally to calcium sulphate and magnesium salts which are held in solution. Calcium carbonate is a by-product in several chemical manufactures, and in this connection it is of use in cement-making. Chalk, the

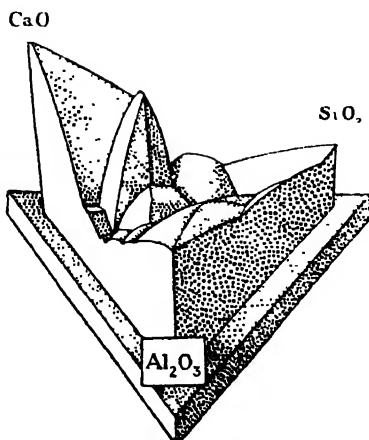
CAO—AL<sub>2</sub>O<sub>3</sub>—SiO<sub>2</sub> PHASE DIAGRAM

CONCENTRATION—TEMPERATURE RELATIONSHIP

Arrows show direction of lower temperature.  
Dotted lines show isotherms in ° C.



1	CaO	8	Ca <sub>3</sub> Al <sub>2</sub> SiO <sub>7</sub>
2	Ca <sub>2</sub> SiO <sub>4</sub>	9	CaAl <sub>2</sub> O <sub>4</sub>
3	Ca <sub>3</sub> SiO <sub>5</sub>	10	Ca <sub>3</sub> Al <sub>10</sub> O <sub>18</sub>
4	Ca <sub>3</sub> Al <sub>2</sub> O <sub>4</sub>	11	SiO <sub>2</sub>
5	Ca <sub>3</sub> Al <sub>8</sub> O <sub>14</sub>	12	CaAl <sub>2</sub> Si <sub>2</sub> O <sub>9</sub>
6	Ca <sub>3</sub> Si <sub>2</sub> O <sub>7</sub>	13	Al <sub>2</sub> O <sub>3</sub>
7	CaSiO <sub>3</sub>	14	Al <sub>2</sub> SiO <sub>5</sub>

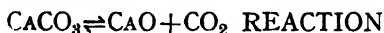


From a photograph of solid model showing temperature relationship of the ternary system CaO—Al<sub>2</sub>O<sub>3</sub>—SiO<sub>2</sub>. (See preceding diagram.)

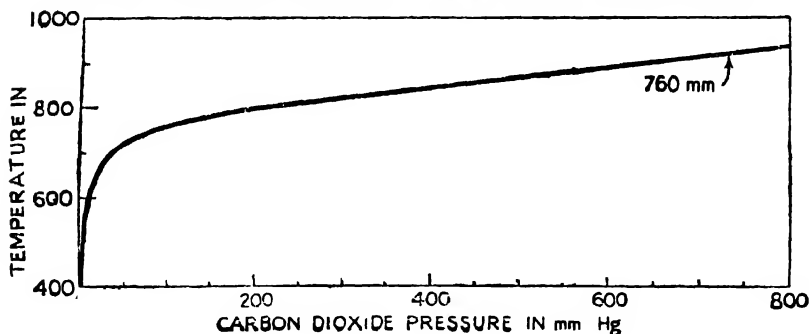
native carbonate of an earthy nature, is used as a dressing for heavy lands and making cement. Precipitated chalk is a well-known form of calcium carbonate, used in the preparation of dentifrices, putty, and pigments, in the glass and paper manufactures, and as a material for stone-dusting of mines. (See also Oölite.)

**Calcium Silicide** — A ferrous metal deoxidizer.

**Calcium Sulphate**, which is practically insoluble in water, occurs in nature and exists in another form, artificially prepared, as monohydrate ( $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ ), of sp. gr. 2.32. From a given pair of precipitants it can also be precipitated either as the dihydrate or the hemihydrate (Smits, *J.S.C.*, 1926, 2655). For technological purposes the gypsum rock, or "gypsite" (an earthy disintegrated rock), is dried in a rotating cylinder, followed by grinding in special mills, screening, calcination, and regrinding. Gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) of sp. gr. 2.96 exhibits great capability to resist fire, and finds considerable employment as a protective material in building construction; also in the paint trade;



CARBON DIOXIDE PRESSURE—TEMPERATURE RELATIONSHIP



as a filling material in paper-making; in the cotton and lace trades to give a finish to certain classes of goods; and as a retarder in the setting of Portland cement, whereas anhydrite is a poor retarder. Anhydrite ( $\text{CaSO}_4$ ) occurs in large quantities in the Hartz Mountains, Upper Italy, in the U.S.A., and elsewhere, and is often found in association with gypsum. It is of crystal system No. 4, cannot be hydrated by heating with water under pressure, but after grinding to colloid form, hydration slowly occurs by keeping wet for some weeks.

**Plaster of Paris** ( $(\text{CaSO}_4)_2 \cdot \text{H}_2\text{O}$ ) is calcium sulphate which has been deprived of part of its water of combination by heating to about  $125^\circ \text{C}$ . It has a great affinity for recombining with more water, with which it sets into a hard mass, and is largely used for lining walls, moulding, and other purposes. The sulphate ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) (sp. gr. 2.3) exists in two crystalline forms, monosymmetric (No. 6) and orthorhombic (No. 5) or labile form, and during heating a period of induction occurs in which the change from the first named to that of the other takes place without loss of water.

Upon heating gypsum from 109° to 130° C. it loses three-fourths of its water and forms the hemihydrate ( $\text{CaSO}_4, \frac{1}{2}\text{H}_2\text{O}$ ), and it is to the reversion of this, by combination with more water, into the form of the dihydrate that plaster of Paris, which is largely made from it, owes its setting powers. This setting is accompanied by a contraction, followed by an expansion due to a change in the crystal system from the monosymmetric system of gypsum into the rhombic type of the dihydrate.

GYPSUM, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country					Gypsum Millions of Metric Tons	
France	..	..	..	..	1.3*	
United Kingdom		..	..	..	1.1	
Germany	..	..	..	..	0.9*	
Italy	..	..	..	..	0.4	
Latvia	..	..	..	..	0.2	
Rumania	..	..	..	..	0.1	
					—	4.0
U.S.A.	..	..	..	..	2.7	
Canada	..	..	..	..	1.1	
					—	3.8
Argentina	..	..	..	..		0.1
British India	..	..	..	..	0.1	
Japan	..	..	..	..	0.1*	
					—	0.2
Egypt	..	..	..	..		0.2
Australia	..	..	..	..		0.2
						—
Sum of above	..	..	..	..		8.5
WORLD PRODUCTION	..	..	..	..		8.8*

\* Estimated.

As ordinarily prepared from gypsum by grinding and calcination by indirect heating there are some small particles of gypsum which have not lost water, and they act as nuclei for the production of new crystals, thus producing feathery arms, or so-called "spherulites," which interlock, and this, with cohesion between the crystals, provides the setting. The temperatures required to convert gypsum into  $\text{CaSO}_4, \frac{1}{2}\text{H}_2\text{O}$  and that substance into  $\text{CaSO}_4$  depend upon several circumstances, the

## CALCIUM

first so-called "boil" covering the first stage, varying from  $108^{\circ}$  to  $130^{\circ}$  C., and the second "boil," completing the dehydration, varying from  $160^{\circ}$  to  $200^{\circ}$  C., the product being known as "anhydrite." From a study of the solubility curves, sub-hydrate below  $98^{\circ}$  C. and anhydrite below  $38^{\circ}$  C. can take up water to form gypsum, and both should be capable of functioning as plasters at normal temperatures.

Calcium sulphate in its various forms is used in the ceramic, paint, and paper industries; also in making statues, busts, "stucco," and polishing powders. Bad plaster-work has been attributed to use of an excess of water for setting. Waste lime and calcium sulphate are utilized to some extent in the manufacture of tiles and the preparation of the composition  $2\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ .

"Stucco" is a coloured form of plaster prepared with a solution of size and used as a wall covering and similar purposes.

**Calcium Carbide** ( $\text{CaC}_2$ ) (sp. gr. 2.22) — When ground lime or chalk is strongly heated with coke in an electric furnace at about  $3,000^{\circ}$  C., calcium carbide is produced, and this product is made on a large scale for use in the preparation of calcium cyanamide and of acetylene gas for welding metals, lighting, and synthetic chemicals. In practice, 1 ton of calcined limestone mixed with 0.7 ton of anthracite is used to produce 1 ton of carbide.

The by-product of its decomposition with water is slaked lime, and this can be utilized in the building trade as a sand lime in mortar making or clinker brick, also as a soil dressing and for causticizing soda-liquors of paper mills. (See Acetylene, and Carbides.)

**Calcium Sulphide** ( $\text{CaS}$ ) exhibits the property of giving out a phosphorescent light in the dark, and is used in the preparation of luminous paint. It is but slightly soluble in water, and when boiled in water it is decomposed, forming the hydroxide  $\text{Ca}(\text{OH})_2$  and the hydrosulphide  $(\text{Ca}(\text{SH})_2)$ —a product which is used for unhairing skins before tanning them.

**Calcium Chloride** ( $\text{CaCl}_2$ ) is made from the still liquors of the ammonia-soda process. It can be obtained in a crystalline form combined with water ( $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ ), which melts at  $29^{\circ}$  C. in its own water, and when heated above  $200^{\circ}$  C. the whole of the water is evolved and the anhydrous compound results. This is very hygroscopic, extremely soluble in water, and is employed for drying coal gas and other gases by passing them over or through vessels packed with it. In one commercial form it is prepared as a solid containing from 70 to 75 per cent., and is used in ice-making, for refrigeration, and in the concrete, cotton, and other trades. It is spread on the surface of roads, where it absorbs moisture from the air thus forming a solution which prevents dust. A spray of calcium chloride solution has been tried in the dissipation of fog over a limited area to increase the safety of airplane landings. Solid calcium chloride is used to remove moisture from air. (See Drying.)

**Calcium Nitrate** ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ) is a white deliquescent substance, soluble in water, and used in pyrotechnics for producing red coloration.

**Calcium Phosphate (Tricalcium Phosphate)** ( $\text{Ca}_3(\text{PO}_4)_2$ ) is the most important of the phosphates of calcium, and occurs in the mineral forms

of *sombrerite*, *coprolites*, and *osteolite* ( $\text{Ca}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ). When acted upon by sulphuric acid it is decomposed, forming a mixture of another phosphate and calcium sulphate known commercially as superphosphate of lime, which is marketed of various strengths. (See Superphosphate.) Calcium phosphate is used in ceramics, enamelling, polishing, and making "milk glass."

**Calcium Biphosphate**, or acid calcium phosphate ( $\text{CaH}_4(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ), is a colourless deliquescent crystalline salt soluble in water, made by reaction between rock phosphate and sulphuric acid. It is used in baking powder in place of cream of tartar.

#### PHOSPHATE ROCK, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country					(Calcium) Phosphate Rock	
					Millions	Metric Tons
U.S.S.R. . . . .	..	..	..	..		1.6*
U.S.A. . . . .	..	..	..	..		3.9
Tunisia . . . . .	..	..	..	..	1.8	
French Morocco . . . . .	..	..	..	..	1.6	
Algeria . . . . .	..	..	..	..	0.6	
Egypt . . . . .	..	..	..	..	0.5	
					—	4.5
Nauru and Ocean Islands . . . . .				..		1.1
Sum of above . . . . .	..	..	..	..		11.1

WORLD PRODUCTION, approximately the above.

\* Estimated.

**Calcium Fluoride** ( $\text{CaF}_2$ ) is found as *fluorspar* in crystalline cubes in Derbyshire and Cumberland, and in Kentucky and Illinois, and is used as a flux in the reduction of metals to impart desirable viscosity to slags, also in the preparation of enamels. When heated with strong sulphuric acid, hydrofluoric acid and calcium sulphate are produced. (See Fluorine.)

**Bleaching-powder** ("chloride of lime") is manufactured on a large scale by the action of chlorine gas upon moist slaked lime (free from iron and magnesium) at not exceeding  $40^\circ\text{C}$ . and until the product contains about from 35 to 38 per cent. of chlorine, the interaction that takes place being represented by the equation  $\text{Ca}(\text{OH})_2 + \text{Cl}_2 = \text{CaOCl}_2 + \text{H}_2\text{O}$ , although there is always an excess of lime left in the resulting product. A special Italian make of bleaching-powder in both the hydrated and anhydrous crystalline forms is prepared by the action of chlorine gas

at 40° C. upon finely divided hydrated lime suspended in carbon tetrachloride and named "Siclor." The manufacture is generally conducted in chambers of various designs in which the lime is exposed on the floor or shelves in layers of varying thickness from a few centimetres upwards, but there are other installations in which rotary action is employed to carry the lime through a tube or over a plane in which it is exposed to the action of the chlorine, and thus made to present fresh surfaces as it moves along. Above 45° C. there is formation of chlorate,

#### FLUORSPAR, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country				Fluorspar Metric Tons
Germany	..	..	..	152,000
France	..	..	..	52,000
United Kingdom	..	..	..	39,000
Italy	..	..	..	13,000
Spain	..	..	..	7,000
Norway	..	..	..	2,000
				<hr/>
				265,000
U.S.S.R.	..	..	..	70,000*
U.S.A.	..	..	..	134,000
Newfoundland	..	..	..	9,000
				<hr/>
				143,000
Korea	..	..	..	20,000
Union of South Africa	..	..	..	6,000
Tunisia	..	..	..	2,000
				<hr/>
				8,000
Sum of above	..	..	..	506,000
WORLD PRODUCTION	..	..	..	512,000*

\* Estimated.

and at 50° C. bleaching-powder begins to decompose rapidly. The available chlorine content suffers loss by storage fairly regularly.

A high test product containing 65 per cent. of available chlorine is obtained by adding pure slaked lime to a clear solution of bleaching-powder (5 to 6 per cent. available chlorine) and evaporating *in vacuo* at 40° C. Bleaching-powder yields, by treatment with water, the normal hypochlorite, and from the solution, the crystallized hypochlorite can be obtained of 90 to 95 per cent. available chlorine by

Kingzett's process of evaporation *in vacuo*. Bleaching-powder occasionally explodes, due to contamination with iron and manganese. Solutions of it are decomposed by small amounts of catalytic agents, such as cobalt, nickel, copper, and iron oxides to yield oxygen gas, and by light.

Bleaching-powder is largely employed in the arts, goods to be bleached being first of all dipped into a dilute solution of the substance and then passed through a dilute acid solution, chlorine gas being thus liberated within the fibres of the fabrics. Apart from its use in the paper and textile trades for bleaching, it is used also on a considerable scale as a sanitary reagent and for refining petroleum oil. Bleaching by chlorine is really a process of oxidation, as the chlorine decomposes water in the act, liberating nascent oxygen; thus indigo blue is converted by chlorine into an orange-red non-tinctorial principle named isatin.

**Calcium Cyanamide** or **Nitro-lime** ( $\text{CaCN}_2$ ) — See Cyanamide.

**Calcium Acetate** ( $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ ) is a white crystalline body, soluble in water, employed in the manufacture of acetone, acetic acid, dyeing, and calico printing. It is marketed also as "Lime Acetate," brown and grey (80 per cent.).

**Calcium Lactate** ( $\text{Ca}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot 5\text{H}_2\text{O}$ ) is colourless, soluble in water, and used in medicine.

**Calcium Arsenate** ( $\text{Ca}_3(\text{AsO}_4)_2$ ), made from calcium chloride and sodium arsenate, is a white poisonous powder, slightly soluble in water, extensively used for eradicating the boll-weevil from growing cotton plants by dusting them at night, 5 to 7 pounds being used per acre, and otherwise as an insecticide and fungicide.

There is an electrolytic process for making this product more economically, in which white arsenic is dissolved in caustic soda and the sodium arsenite solution thus produced is converted into sodium arsenate by electrolytic treatment, after which, by treatment with hydrated lime in water, calcium arsenate is produced. It is alleged that calcium arsenate as thus made acts better than that otherwise made, for dusting on cotton plants, by reason of its greater adhering character. It is stated that the toxicity of calcium arsenates decreases with increase in the molecular ratio  $\text{CaO} : \text{As}_2\text{O}_3$  in combination, and that the acid arsenates are much more toxic than the basic ones.

**Calcium Bisulphite** ( $\text{Ca}(\text{HSO}_3)_2$ ) is soluble in water, and is prepared in the form of a yellowish liquid, having a strong odour of sulphur dioxide, by the action of that gas on calcium hydroxide or carbonate, the product being generally sold of sp. gr. 1.070 or 9° Bé strength under the name of lime bisulphite. It is largely used in the manufacture of wood pulp, as the principal constituent in the cooking liquor of the "sulphite" process, also as an antichlor, as a preservative, and for bleaching sponges.

**Calcium Borate** — See Pandermite.

**Calcium Citrate** ( $\text{Ca}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 4\text{H}_2\text{O}$ ) — This salt is soluble in cold water, but nearly insoluble in hot water. (See Citric Acid.)

**Calcium Caseinate** — A preparation used for increasing the wetting and penetrating power of horticultural washes, thereby improving their insecticidal and fungicidal efficiency, as in the control of *Woolly Aphis*. Experience has shown that a 0.2 per cent. solution appears to be the lowest strength required to reduce the surface tension to a minimum, and give maximum spreading and wetting effect. (See Insecticides.)

**Calcium Chlorate** ( $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{H}_2\text{O}$ ) is a nearly white crystalline compound prepared by action of chlorine upon calcium hydroxide (milk of lime) at above  $45^\circ \text{C}$ . ; soluble in water and used in making pyrotechnics for producing red coloration, and as a constituent of the weed-killing compound named "Weedex."

**Calcium Permanganate** ( $\text{Ca}(\text{MnO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) — A violet crystalline salt, used for sterilizing, disinfecting, and in the textile trade.

**Calcium Phosphide** ( $\text{Ca}_3\text{P}_2$ ) — A grey substance obtained by heating calcium phosphate and aluminium. It is decomposed by water, thus generating hydrogen phosphide, which takes fire in air. (See Phosphorus.)

**Calcium Tungstate** ( $\text{CaWO}_4$ ) — A crystalline substance, insoluble in water, used in radiography, and making luminous paint. (See Tungsten.)

**Calcium Molybdate** ( $\text{CaMoO}_4$ ) — A white crystalline powder insoluble in water, but soluble in acids, made by fusing molybdenum ores with lime; used for making molybdic acid and as a substitute for ferromolybdenum in the manufacture of steel. According to H. C. Mabbe, it can be easily made for use in steel manufacture by roasting molybdenite at  $600^\circ \text{C}$ . until free from sulphur and then heating the resulting trioxide at  $600^\circ \text{C}$ . with finely powdered calcium carbonate.

"**Lime-sulphur**" (made from lime, sulphur, and water) is used as an insecticide and fungicide.

There are commercial preparations of **calcium sulphite** (in powder and tablets) and **calcium ferrocyanide**; while **calcium silicate** is now prepared in the form of grey pressed bricks.

**CALCULI (Urinary)** — Concretions in the bladder consisting of or containing uric acid, ammonium and other urates, calcium oxalate, calcium phosphate, the double phosphate of ammonium and magnesium, xanthine and cystine, generally constructed round a nucleus of some foreign substance, such as blood-corpuscles.

"**CALEDON**" **DYES** — A collective term for dyes of various types, including "Solway," "Caledon," "Celatene," and "Soledon."

**CALENDERING** — The application of heavy continuous pressure with heating during the finishing of paper and textiles resulting in a lustrous surface.

**CALENDULA** — See Marigold.

"**CALGON**" — A proprietary water-softener containing sodium hexametaphosphate.

**CALICHE (Chile Nitre)**— This impure "soda nitre" (sodium nitrate) occurs in almost unlimited quantities in South America, especially Chile and the district of Atacama in Peru, the average content of sodium nitrate being about 25 per cent. New South African deposits containing on an average about 16 per cent. sodium nitrate have been found in the Gibeon district some fifty miles to the east of Mariental on the railway towards the Kalahari Desert. According to one view, the origin of caliche is to be attributed to the transformation of the large quantities of ammonium chloride which impregnate the ash of Chilian volcanoes, the bacterial nitrification being intensified by radioactivity. It is cheaper than potassium nitrate, and yields 9 per cent. more nitric acid when employed for the manufacture of sulphuric acid. Large amounts were used in the explosives and agricultural industries until the successful competition of nitric acid made by synthetic processes. (See Nitrogen Fixation.)

The following analyses have been published :

	No. 1, White Caliche				No. 2, Brown Caliche			
	Per Cent.				Per Cent.			
Sodium nitrate .. .. .				70.62				60.97
„ iodate .. .. .				1.90				0.73
„ chloride .. .. .				22.39				16.85
„ sulphate .. .. .				1.80				4.56
Calcium sulphate .. .. .				0.87				1.31
Magnesium sulphate .. .. .				0.51				5.88
Insoluble matter .. .. .				0.92				4.06
Water .. .. .				0.99				5.64
				100.00				100.00

Caliche is often found covered by deposits of *costra*, which is a harder saline deposit of less value. It is reported that average Chilian caliche contains 0.15 per cent. iodine in the form of sodium iodate.

**CALICO PRINTING**— The art of imprinting colours on cotton cloth or calico with dyes, the spreading being prevented by the use of thickening agents, such as gum, starch, paste, etc., added to the dye. The name calico is derived from Calicut, a town in the Indian district of Malabar, where at one time calico printing was practised. Hollow copper rollers are used for the printing, the patterns being etched on the cloth, and the colours being carried by films on the rollers by passing through the colour boxes suitably arranged. Machines are made by means of which as many as sixteen different colours can be printed at one time.

Mordants are used for fixing the colours as may be necessary, and a dressing or "finished" appearance is given to the cotton goods by treatment with some adhesive, such as starch or dextrine; "weighting" being given by admixture of barium sulphate, gypsum, or china clay etc.

**CALIFORNIUM** (Cf) — Element 98, announced in March, 1950, by Glenn T. Seaborg, S. G. Thompson, Albert Ghiorso, and Kenneth Street, Jr., of the University of California, Berkeley. Produced by the irradiation of a minute quantity of curium with cyclotron alpha particles having an energy of 35 million electron volts. Its half-life is only 45 minutes, and it is a homologue of dysprosium (element 66).

“**CALLACTITE**” — A colloid acid-proof material prepared from hard pitch by dispersing it in a ball mill with an equal volume of water in association with from 0.1 to 0.25 per cent. of resin soap. The resulting product is then mixed with about an equal quantity of asbestos or cellulose fibre pulp, thus coagulating the pitch upon the fibre, after which the product is fashioned into sheets on a paper machine, and these are compressed while in a heated state. It is described as a material which can be manipulated without splitting or cracking, is a good electrical insulator, is acid-proof, and can be used as a roofing material.

**CALOMEL** (Mercurous Chloride) — See Mercury Compounds.

**CALORIE** — The 15-degree calorie (the heat required to raise one gram of water from 14.5° to 15.5° C.) is equivalent to 4.1855 absolute joules. One kilogram calorie (Kg-cal.) is one thousand times the unit calorie.

**CALORIFIC VALUE** — The amount of heat evolved by combustion of a unit quantity of substance, for example, coal, under standardized conditions, and expressed in calories per gram or in British Thermal Units per pound. (See Heat.)

**CALORIMETER** — Apparatus for measuring the heat changes in chemical interactions. There are several forms, a common one consisting of a metal vessel immersed in water, which is warmed or cooled accordingly. Particular appliances of this kind, useful for determining the calorific values of fuels, are known as the “Berthelot-Mahler” “Scholes,” and “Emerson” bomb calorimeters. The “Simmance,” “Sargent,” and “Thomas” are among the best-known gas calorimeters. (See *The Modern Calorimeter*, by W. P. White (Reinhold Publishing Corp., New York.)

**CALORIZING** — See Metals.

**CALUMBA** — The dried root of *Jateorhiza palmata*, cut into transverse or oblique slices. The plant grows in Portuguese East Africa and the forests near the Zambesi. Calumba contains a number of bitter principles including columbamine, palmatine, and jateorhizine. Used in medicine as a stimulant to the appetite.

**CALX** — The residual matter resulting from the calcination of mineral matter.

**CAMOMILE** — See Chamomile.

**CAMPHENE** (C<sub>10</sub>H<sub>16</sub>) — A colourless, crystalline terpene of sp. gr. 0.8446, m.p. 43° C., b.p. 159° C. of dextro, lævo, and inactive forms; prepared by treating bornyl chloride with alcoholic potash. It does yield camphoric acid when subjected to the action of nitric acid,

because the camphane bridge ring isomerises into the camphene bridge by the rupture of carbon to carbon bonds. It is soluble in alcohol and ether, and is used in making camphor substitutes. (See Terebene.)

**CAMPBOR** ( $C_{10}H_{16}O$  or  $C_9H_{14}CO$ ) — A ketonic derivative of the dicyclo-monoölefin series of terpenes, formerly obtained entirely from the camphor tree (*Cinnamomum Camphora*) grown mainly in Formosa. It is obtained by distilling the wood of the trees, and purifying the product by sublimation. A product of the distillation is camphor oil (see same), which is a mixture of terpene hydrocarbons.

Camphor is soluble in alcohol, and ether, crystallizes in glistening prisms, m.p.  $179^{\circ}C.$ , b.p.  $209^{\circ}C.$ , sp. gr. 0.986 to 0.996, and can be readily sublimed. By reduction it yields cymene ( $C_{10}H_{14}$ ), and by oxidation with nitric acid it yields dibasic camphoric acid ( $C_8H_{14}(COOH)_2$ ). Most natural camphor is dextro-rotatory but a laevo form occurs in *Matricaria Parthenium*.

Synthetic camphor is made industrially from pinene ( $C_{10}H_{16}$ ), the chief constituent of German and American turpentine. Pinene is treated with hydrogen chloride gas, and the white, crystalline bornyl chloride resulting is converted through camphene to isobornyl acetate, which is then oxidized to camphor.

Camphor is used in large quantities in the manufacture of celluloid, and in medicine as a counter-irritant and carminative, and by injection as a restorative. Either natural or synthetic products can be used as the dextro-rotatory form does not differ physiologically in action from the optically inactive manufactured form.

*Reference*: I. Gubelmann and H. W. Elley, "American Production of Synthetic Camphor from Turpentine," in *Ind. Eng. Chem.*, **26**, 589 (1942).

**CAMPBOR OIL (Rectified Oil of Camphor)** — The lower boiling fractions obtained as a by-product in the manufacture of camphor from crude camphor oil from *Cinnamomum camphora*. It contains about 35 per cent. of cineole together with safrole, *d*-pinene, eugenol, phellandrene, and camphor; soluble in alcohol and ether; sp. gr. 0.875 to 0.900, at  $15^{\circ}C.$ ; ref. ind. 1.465 to 1.470 at  $20^{\circ}C.$  Used in perfumery and in medicine as a rubefacient.

**CAMPBOR WOOD OIL** is sometimes supplied in the form of a yellow crystalline mass, soluble in alcohol and ether, but otherwise as a liquid, and is furnished by dry distillation of the camphor-tree wood (*Dryobalanops aromatica*). It is used in perfumery.

The oil distilled from the leaves of Indian-grown trees contains pinene, dipentene, safrol, cineol, terpineol, and caryophyllene, but cineol is stated to be absent from the oil distilled from the twigs. The wood oil is stated to be similar to that produced elsewhere; it contains safrol, eugenol, carvacrol, and other substances, but not cineol, and is used in Japan as raw material for the manufacture of heliotropin from the safrol contained in it.

**CAMPHORIC ACID** ( $C_{10}H_{16}O_4$  or  $C_8H_{14}(COOH)_2$ ) is prepared by the oxidation of camphor ( $C_{10}H_{16}O$ ) with strong nitric acid, and is a white

crystalline dibasic acid, slightly soluble in cold water, fairly so in hot water, easily dissolved by alcohol, and used in making celluloid articles. Modifications of it include four optically active (all with specific rotations about  $48^\circ$ ). The *d*- and *l*-camphoric acids, m.p.  $187^\circ\text{C}$ ., form anhydrides—they are *cis* forms—and the *d*- and *l*-isocamphoric acids, m.p.  $171^\circ\text{C}$ ., do not form anhydrides—they are *trans* forms) and two optically inactive forms, m.p.  $202^\circ\text{C}$ .

**CAMWOOD** — See Barwood.

**CANADA BALSAM** — See Balsams.

**CANANGA OIL** — See Ylang Ylang Oil.

**CANDELILLA WAX** — See Waxes.

**CANDLEBERRY WAX (Bayberry)** — See Waxes.

**CANDLE-NUT OIL (Lumbang Oil)** — Made in the Philippine Islands from the fruits of the candleberry tree (*Aleurites moluccana* and *A. tri-sperma*). The kernels yield an oil of marked drying quality, making up 63·7 to 66 per cent. of their weight. It is liquid at  $18^\circ\text{C}$ ., of pale yellow colour, sp. gr. at  $15^\circ\text{C}$  0·928, acid value 1·3, sap. v. 195, i. v. 138, ref. ind. at  $40^\circ\text{C}$  1·4703; used in the paint, varnish, and soap trades, also as an illuminant and sometimes as an adulterant of tung oil, but is not edible on account of its purgative properties. The oil is stated to have the following ester composition: glyceryl linolenate 6·5 per cent., glyceryl linolate 33·4 per cent., glyceryl oleate 56·9 per cent., glycerides of solid acids 2·8 per cent.; to behave much like linseed oil upon oxidation; and the residual cake left after extraction of the oil is valuable as a fertilizer of high nitrogen content (7 to 9 per cent.).

**CANDLES** are made of tallow, palm oil, or other solid fats, and paraffin wax in various proportions, and are provided with plaited wicks, which are self-trimming in the flame. Paraffin wax or ozokerite increases the hardness of candles.

**CANE SUGAR** — See Sugar.

**CANE WAX** — See Waxes (Sugar Cane).

**CANELLA BARK** — Of the *Canella alba*, or so-called wild cinnamon tree (West Indian Islands), belonging to the gamboge order (Clusiaceæ); imported from the Bahamas.

**CANELLA OIL** — A colourless spicy oil, distilled from the bark of *Canella alba* (of the gamboge order), resembling clove and cajuput oils in odour; containing eugenol, cineol, etc.; sp. gr. 0·92 to 0·935; soluble in alcohol, etc., and used in medicine; yield is 1 per cent.

**CANNABIS (Indian Hemp)** — The dried flowering and fruiting tops of the pistillate plant of *Cannabis sativa*, a herb indigenous to central Asia and cultivated in India, Africa, and North America. It contains a resin which is used as a constituent of corn paints and which, if administered internally, produces at first a feeling of excitement followed by deep sleep. The principal constituent of the resin is an

alcohol, cannibinol,  $C_{21}H_{40}O_2$ , a reddish oily liquid which resinifies on exposure to air. The drug itself is known as haschisch and is used in some Eastern countries (Turkey, Arabia, and Egypt) for chewing. An electuary prepared from cannabis has also been known as haschisch. The drug from which the gum-resin has been extracted is known as "charas" or "churrus" and is used in the East for smoking. Preparations of cannabis are included in the schedule of dangerous drugs subject to control by international agreement. (See Wollner *et al.* on "The Isolation of Tetrahydro-cannabinol from Cannabis" in *J. Amer. Chem. Soc.*, **64**, 26 (1942); Levine, *J. Amer. Chem. Soc.*, **66**, 1868 (1944); *Brit. Med. J.*, **1**, 918 (1947); and Lowe on the physiological activity of cannabis in *Science*, **102**, 615 (1945).)

**CANTHARIDES (Spanish Fly)** — The dried beetle, *Cantharis vesicatoria* (Order Coleoptera; Fam. Meloidæ) which is collected in South Russia, Galicia, Rumania, Italy, and Spain. It contains an active principle, cantharidin ( $C_{10}H_{12}O_4$ ), a poisonous, crystalline lactone which is insoluble in water, but soluble in chloroform and acetone and has a m.p. of 216° to 218° C.

Cantharidin is prepared from cantharides or from the Chinese insect, *Mylabris cichorii*, by digestion with ether or alcohol or a mixture of these solvents. The American "Blister Beetle" (*Marcobasis albida*, Say) is stated to yield from the dried material by direct sublimation from 0.6 to 1 per cent. of free cantharidin and 4 to 5 per cent. of total cantharidin.

Cantharidin is used in medicine as a vesicant in the form of a solution in acetic acid or as a plaster. It has also been used in hair tonics.

**CAOUTCHOUC** — See Rubber.

**CAPE** — See Gums and Resins.

**CAPILLARY ATTRACTION**, or surface tension effect, depends upon the adhesion or cohesion of fluids to solids, and is closely akin to adsorption, as instanced by a burning night-light in which the melted wax flows to the burning wick. Water is supplied to the roots and stems of growing plants by capillary attraction. Capillary attraction is also defined as the natural tendency of liquids to contract to a minimum. (See Colloid Chemistry, Lubrication, and Surface Tension.)

**CAPRIC ACID** ( $C_8H_{16}.COOH$ ) — A member of the normal fatty acids, present in cow's and goat's milk, and coconut oil, and formed by the oxidation of oleic acid; m.p. 31.5° C., b.p. 269° C. It is soluble in alcohol.

**CAPROIC ACID** ( $C_6H_{11}.COOH$ ) — A member of the normal fatty acids contained in goat's milk and coconut oil; often forms one of the products of the oxidation of higher acids of the same series. It is a colourless oily body of m.p. -1° C., b.p. 202° C., sp. gr. 0.928, with a sudorific odour, and is soluble in alcohol and ether.

"CAPROKOL" — See Hexylresorcinol.

**CAPRYLIC ACID** ( $C_7H_{15}.COOH$ ) — A member of the normal fatty acids present in cow's milk, goat's butter, coconut oil, Limberg cheese, and some fusel oils; sp. gr. 0.910, m.p.  $16^{\circ}C.$ , b.p.  $237.5^{\circ}C.$ ; soluble in water, alcohol, and ether.

**CAPSICUM** (Cayenne Pepper, Chillies, Red Pepper) — The dried ripe fruit of *Capsicum minimum* (Solanaceæ), indigenous to tropical America and cultivated in Africa, South America, and other tropical countries. It contains a colourless, crystalline, pungent principle, capsaicin,  $C_{18}H_{27}O_3N$ , of m.p.  $64.5^{\circ}C.$  The name "capsicine" has been applied in America to an oleo-resin extracted from *Capsicum baccatum*. Japanese Chillies, derived from *Capsicum frutescens*, are brighter in colour than the African variety but possess about only one-quarter the pungency. Bombay Chillies are obtained from *Capsicum annuum*, which is also the source of Paprika in Hungary and Spanish pepper.

**CAPSULARIN** — See Glycosides.

**CAPTURE** — A term referring to any process in which a neutron, upon collision with an atomic nucleus, (1) sticks to it, (2) is absorbed into it, or (3) causes fission. (See Nuclear Chemistry.)

**CARAGHEEN MOSS** — See Sea-weeds.

**CARAMEL** — A dark-coloured substance, soluble in water, made from cane-sugar by heating above its melting-point ( $160^{\circ}C.$ ) up to about  $180^{\circ}$  to  $190^{\circ}C.$  (or from glucose by heating to  $198^{\circ}C.$ ), when it is said to lose two molecules of water and caramelan ( $C_{12}H_{18}O_9$ ) is formed—a brown colouring matter which is the characteristic principle of caramel or sugar dye. It can also be prepared by the action of a strong solution of potassium or sodium hydroxide upon glucose solution, and again by heating starch syrup, glucose, molasses, etc., with 10 per cent. glacial acetic acid and acetic anhydride or sodium acetate under reflux, precipitating the caramel thus formed by means of sodium carbonate (U.S. Patent, No. 1,316,019). The so-called "ammonia process" for the manufacture of caramel consists in bringing ammonia in the form of gas or strong solution into contact with fused dextrose or dextrose in solution at a temperature of from  $35^{\circ}$  to  $40^{\circ}C.$ , when combination occurs, resulting in the formation of glucose-ammonia, and when the ammonia is removed by heating to  $100^{\circ}C.$ , a mixture of aldoses and ketoses in equilibrium is formed. Ammonia reacts much more vigorously with lævulose solutions than with those of dextrose, and the reaction is accompanied by instantaneous darkening and decomposition. Caramel is used as a colouring and flavouring material and in confectionery.

**CARAT** — For gold, a content of pure gold in alloys of one-twenty-fourth part per carat, thus, 18 carat gold contains 18 parts by weight of pure gold in 24 parts by weight of the alloy. For diamond and precious stones, 200 milligrams per metric carat (legal).

**CARAWAY OIL**—A pale yellow essential oil obtained by distilling the crushed seeds of *Carum Carvi* (indigenous in Holland and grown in Moravia and Germany), soluble in alcohol and ether, containing about 58 per cent. carvone and some *dextro*-limonene. Sp. gr., 0.91 to 0.92 at 15° C.; opt. rot., +70° to +80°; ref. ind., 1.485 to 1.492 at 20° C.; used in medicine, perfumery, and in flavouring.

**CARBACHOL** ("Doryl," "Moryl") ( $C_8H_{15}O_2N_2Cl$ ) — A colourless, crystalline compound, namely, carbamylcholine chloride,  $(H_2N.CO.OCH_2.CH_2N(CH_3)_3)Cl$ ; soluble in water; slightly soluble in alcohol; insoluble in acetone and ether; m.p. 210° to 212° C. It has a physiological action similar to acetylcholine and is used in medicine as a cholinergic drug. (See Acetylcholine.)

**CARBAMIDE** — See Urea.

**CARBARSONE** ("Leucarsone") ( $C_7H_9O_4N_2As$ ) — A white organic compound of arsenic, namely, *p*-carbamidophenylarsonic acid; slightly soluble in water and alcohol; insoluble in ether and chloroform; m.p. about 190° C. It contains 28.5 per cent. of arsenic, and is used in medicine for the treatment of amœbic dysentery.

**CARBAZOLE** (Carbozol) ( $C_6H_4)_2NH$ ), the imide of diphenyl, is a constituent of coal-tar and crude anthracene. It is a white, crystalline substance of m.p. 245° C., b.p. 355° C.; is readily sublimable, and can be formed by passing the vapour of diphenylamine or *o*-xenylamine through red-hot tubes. Carbazole may be separated from crude anthracene by fusing with caustic potash when carbazole-potassium is formed from which the anthracene can be distilled away. On treatment with water the residue regenerates carbazole. This separation is, however, preferably effected by extracting crude anthracene with heavy coal-tar pyridine (b.p. 140—180° C.) in which solvent carbazole dissolves more readily than anthracene. Carbazole is soluble in alcohol and ether, but insoluble in water, and is used in the manufacture of dyestuffs.

**CARBIDES** — Compounds of carbon with metals and non-metals such as aluminium carbide ( $Al_4C_3$ ), calcium carbide ( $CaC_2$ ), cast-iron (a quality of which can be made corresponding with the formula  $CFe_2$ ), and silicon carbide (SiC). Many can be made by heating the metals or their oxides with carbon, and fused metallic carbides are good conductors of electricity. (See Abrasives, and Calcium Carbide.)

**CARBINOLS** — All substances derived from methyl alcohol by exchanging one or more of the hydrogen atoms attached to the carbon atom for any radical or radicals, therefore, ethyl alcohol,  $CH_3.CH_2OH$ , is monomethyl carbinol, isopropyl alcohol,  $(CH_3)_2CHOH$ , is dimethyl carbinol, and tertiary-butyl alcohol,  $(CH_3)_3COH$ , is trimethyl carbinol. Methyl alcohol itself was formerly known simply as "carbinol," now as methanol.

**"CARBITOL"** (UCC) — Trade-mark for glycol-ether type of solvents for cellulose esters and ethers, natural and synthetic resins, and gums. (See Monoethyl, Monobutyl, and Monomethyl Ethers of Diethylene-glycol.)

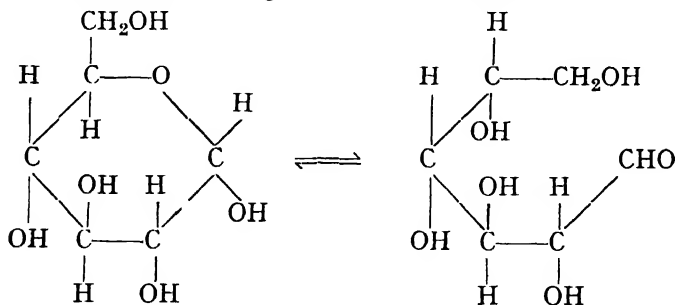
**"CARBOBRONZE"** — An alloy of about 92 per cent. copper, 8 per cent. tin, and 0.3 per cent. phosphorus; used in the dyeing, tanning, and some other industries.

**CARBOCYCLIC** — See Cyclic.

**"CARBOGEN"** — See Carbon Oxides.

**CARBOHYDRATES** — The name given to a large body of organic compounds of great value as foods, so called because it was formerly believed that they all had the formula  $C_x(H_2O)_y$ , *i.e.*, they were believed to be hydrates of carbon. It is now known that many of them cannot be represented by the above formula, but the name persists. The group includes all the sugars, starches, celluloses, and hemicelluloses, and all are polyhydroxy compounds. They fall into the following groups:—

(1) **Monosaccharides** : These are all those simple sugars which cannot be hydrolysed into simpler substances, and are known as tetroses, pentoses, hexoses, etc., according to the number of carbon atoms contained in the molecule. Most of the naturally occurring monosaccharides are pentoses or hexoses, and can be represented by the general formulæ  $C_5H_{10}O_5$ , and  $C_6H_{12}O_6$ , respectively. Further, the group is divided into aldoses of the formula  $CH_2OH.(CHOH)_4CHO$ , such as glucose, mannose, galactose, etc., and ketoses, of the general formula  $CH_2OH.(CHOH)_3CO.CH_2OH$ , such as fructose and sorbose. Arabinose,  $CH_2OH.(CHOH)_3CHO$ , is an example of an aldo-pentose. Although most of their reactions can be satisfactorily explained by the open-chain formulæ depicted above, there are some reactions, such as the formation of the glycosides (see same), which necessitate a different formulation, and it is now known that, at any rate in solution, the monosaccharides have a ring structure, as indicated below



D-Glucose (Ring Form)

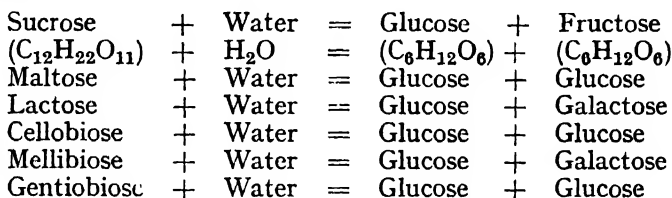
D-Glucose (Open-chain Form)

There is an equilibrium in solution between the two forms, but only a small percentage exists in the open-chain form, and when this form is removed in a chemical reaction, then the ring form isomerises into the

open-chain form until all the sugar is used up. That is to say the two mutually interconvertible forms form a tautomeric system.

All monosaccharides are soluble, sweet, and difficult to crystallize. The most ubiquitous and the most important is glucose, known as D(+)-glucose, or dextrose. Fructose, or fruit-sugar, is known as D(-)-fructose, the "D" indicating its relationship to D-glucose, while the (-) shows that its solutions are laevorotatory to polarized light. This convention is employed in describing all the sugars. Although many of the monosaccharides have been synthesized, their syntheses are not yet commercial propositions, but there is a probability that in the not too distant future glucose will be obtained from wood in worthwhile yields.

(2) **Disaccharides** : This group comprises all those sugars, each molecule of which can be converted, by enzyme action or acid hydrolysis, into two identical or different monosaccharides. The following list includes the most common disaccharides and their hydrolytic products :—



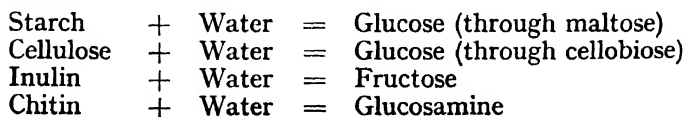
All these hydrolyses may be represented by the formula given for the hydrolysis of sucrose. Although water is necessary for the hydrolysis of disaccharides, it must be realized that a catalyst (not appearing in the equation) is also required, the hydrolysis being extremely slow in pure water.

The disaccharides are further subdivided into (a) non-reducing sugars, such as sucrose, which do not reduce Fehling's solution until after hydrolysis, and (b) most of the others, which reduce Fehling's solution, even before hydrolysis into monosaccharides.

All disaccharides are sweet-tasting, and are easier to crystallize than the monosaccharides. The most important is, of course, sucrose or common sugar, which has the largest production of any organic compound in the world.

Tri-, and tetrasaccharides also exist, but are somewhat rare.

(3) **Polysaccharides** : This important group contains starch, chitin, inulin, and the celluloses. They are all insoluble in water, tasteless, and in their natural states non-crystalline. Specific enzymes or prolonged treatment with acids convert them into first simpler polysaccharides, and then into disaccharides, and finally into monosaccharides, as follows :—



## III. BENZENOID RELATIONSHIPS

Benzene $C_6H_6$	Phenol $C_6H_5OH$		
	Dihydroxy Phenol (1) $HO.C_6H_4.OH(4)$	Benzoquinone (1) $O : C_6H_4 : O(4)$	
Toluene $C_6H_5.CH_3$	Benzyl Alcohol $C_6H_5.CH_2OH$	Benzaldehyde $C_6H_5.CHO$	Benzoic Acid $C_6H_5.COOH$
Diphenylmethane $(C_6H_5)_2CHOH$	Diphenylcarbinol $(C_6H_5)_2CHOH$	Benzophenone $(C_6H_5)_2CO$	
Triphenylmethane $(C_6H_5)_3CH$	Triphenylcarbinol $(C_6H_5)_3COH$		
Tetraphenylmethane $(C_6H_5)_4C$			

## IV. OLEFIN AND ACETYLENE RELATIONSHIPS.

Ethane $\begin{array}{c} CH_3 \\   \\ CH_3 \end{array}$	Ethylene $\begin{array}{c} CH_2 \\ \cdots \\ CH_2 \end{array}$	Acetylene $\begin{array}{c} CH \\ \cdots \\ CH \end{array}$	Ketene Carbomethene $\begin{array}{c} CH_2 \\ \cdots \\ CO \end{array}$
		$\left[ \begin{array}{c} \text{Vinyl Alcohol} \\ CH_2 \\ \cdots \\ CHOH \end{array} \right]$	
	Ethyl Alcohol $\begin{array}{c} CH_3 \\   \\ CH_2OH \end{array}$	Acetaldehyde $\begin{array}{c} CH_3 \\   \\ CHO \end{array}$	Acetic Acid $\begin{array}{c} CH_3 \\   \\ COOH \end{array}$

V. MULTIPLE AND MIXED  $\equiv C-O-C\equiv$  RELATIONSHIPS

(Oxygen-function organic compounds in which C-atoms are joined through O-atom.)

Diethyl Ether $\begin{array}{c} CH_3.CH_3 \\ \diagup \quad \diagdown \\ O \\ \diagdown \quad \diagup \\ CH_3.CH_3 \end{array}$	Acetic Anhydride $\begin{array}{c} CH_3CO \\ \diagup \quad \diagdown \\ O \\ \diagdown \quad \diagup \\ CH_3CO \end{array}$
Ethyl Acetate (Ester) $\begin{array}{c} CH_3CO \\   \\ O-CH_2.CH_3 \end{array}$	
Oils ; Fats ; Waxes	
Ethylidene Diethyl Ether (Diacetal) $CH_3CH(OC_2H_5)_2$	Ethylidene Diacetate $CH_3CH(OOC.CH_3)_2$

VI. MULTIPLE AND MIXED  $\begin{array}{c} =\text{C}-\text{O}- \\ | \\ =\text{C}-\text{O}- \end{array}$  RELATIONSHIPS

(Oxygen-function organic compounds in which C-atoms are directly joined.)

Ethylene Glycol



Glyoxal



Oxalic Acid



Ethylene Oxide



Glycolic Acid

Hydroxyacetic Acid



Glycolic Aldehyde

Hydroxyacetaldehyde



Glyoxylic Acid

Glyoxalic Acid



Carbohydrates

Benzoïn



Hydrobenzoïn



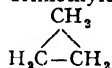
Benzil



VII. CYCLIC  $\equiv\text{C}-\text{O}-\text{C}\equiv$  RELATIONSHIPS

Cyclopropane

Trimethylene



Cyclobutane

$\text{H}_2\text{C}-\text{CH}_2$

$\text{H}_2\text{C}-\text{CH}_2$

$\text{H}_2\text{C}-\text{CH}_2$

Cyclopentane

$\text{H}_2\text{C}-\text{CH}_2$

$\text{H}_2\text{C}-\text{CH}_2$

$\text{H}_2\text{C}-\text{CH}_2$

$\text{CH}_2$

Furan

$\text{HC}-\text{CH}$

$\parallel \quad \parallel$

$\text{HC} \quad \text{CH}$

$\diagup \quad \diagdown$

$\text{O}$

Gamma-Pyrone

$\text{C}=\text{O}$

$\diagup \quad \diagdown$

$\text{HC} \quad \text{CH}$

$\parallel \quad \parallel$

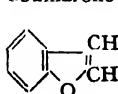
$\text{HC} \quad \text{CH}$

$\diagup \quad \diagdown$

$\text{O}$

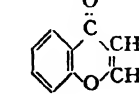
Benzofurane

Coumarone

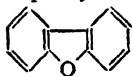


Benzopyrone

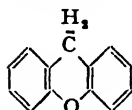
$\text{O}$



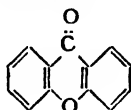
Dibenzofurane  
Diphenylene Oxide



Xanthine



Dibenzylpyrone  
Xanthone



For Chlorine-Containing Organic Substances, see Chlorine.

For Nitrogen-Containing Organic Substances, see Nitrogen.

For Phosphorus-Containing Organic Substances, see Phosphorus.

For Sulphur-Containing Organic Substances, see Sulphur.

The diamond is converted into graphite in the heat of the electric arc, and according to Lebeau and Picon the transformation *in vacuo* occurs between 1,500° and 1,900° C., while above 2,000° C. the change is much more rapid.

Colourless diamond has a determined heat of combustion 94.48 kilocalories per gram atom. When strongly ignited, diamonds burn in the presence of air or oxygen forming carbon dioxide, just as charcoal does at a lower temperature, thus proving that each consists of carbon.

**Graphite** (crystal system No. 3 and sp. gr. 2.2 to 2.3) is found plentifully in nature in Austria, Bohemia, Canada, Japan, Siberia, Spain, California, Ceylon, Germany, India, Italy, Korea, Mexico, Madagascar, Greenland, Moravia, the U.S.A., Russia, the Kenya Colony, and elsewhere, including Grampound in Cornwall and Borrowdale in Cumberland where it is used in making pencils, although the Keswick pencil works use imported graphite. Graphite is a shiny, soft, nearly black substance, consisting largely of carbon (varying from 50 to 97 per cent.), and on account of its refractory character is used for the manufacture of so-called plumbago crucibles—that is, crucibles made of fire-clay mixed with graphite—employed for making “crucible steel,” various alloys, etc. It is also employed for making arc-light carbons; as a polish and coating (black-leading) for iron articles to prevent rusting; in admixture with rubber as an acid-proofing coating, and as a paint pigment and lubricant.

In a pure form graphite can be obtained by the carbonization of artificial silk threads in an atmosphere of coal-gas, and subsequent heating to incandescence at from 1,500° to 2,000° C., when surrounded by either a gaseous or liquid hydrocarbon or hydrocarbon derivative such as hexachlorobenzene at 3 mm. mercury pressure, or carbon tetrachloride at 15 mm. pressure, followed by finally heating to about 3,500° C. in carbon monoxide. The resulting filaments can be bent like lead. Graphite has a determined heat of combustion, 94.03 kilocalories per gram atom.

Carbon is also known in impure **amorphous forms** as a constituent of coke, wood charcoal, lamp-black, and animal charcoal (bone-black), and this last-named substance is used as a decolorizing agent in refining sugar, glycerine, fats, etc., having the property of taking up many kinds of colouring matters. (See Bone-Black.) All these materials are made by pyrolysis, that is, the heating to a high temperature of the material out of free contact with air, provision being made for the escape of volatile materials that are formed during the treatment.

### GRAPHITE (NATURAL), WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country				Graphite Metric Tons	
Germany-Austria	..	..		38,300	
Italy	..	..	..	5,500	
Czechoslovakia	..	..	..	5,000*	
Norway	..	..	..	3,900	
				<hr/>	52,700
Mexico	..	..	..	10,200	
U.S.A.	..	..	..	4,000*	
Canada	..	..	..	1,600	
				<hr/>	15,800
Korea	..	..	..	57,400	
Ceylon	..	..	..	17,500	
British India	..	..	..	700	
				<hr/>	75,600
Madagascar	..	..	..	13,000	
French Morocco	..	..	..	500	
				<hr/>	13,500
Sum of above	..	..			<hr/> 157,600

WORLD PRODUCTION, approximately the above.

\* Estimated.

Natural graphite is also produced in France, Japan, U.S.S.R.

**Coke.** See same.

**Charcoal** (which has been shown to be really crystalline in structure) has the property of adsorbing gases very readily, particularly when cooled, wood and peat charcoal being superior in this respect to animal charcoal. The adsorptive power of wood charcoal is notably increased by prolonged heating, and the denser charcoals—notably those from

palm-nut, coconut, and fruit stones—are the most efficient gas adsorbents. The following table shows the capacity of adsorption of various gases by boxwood charcoal :

Ammonia gas	..	..	..	..	90 volumes.
Hydrochloric acid gas	..	..	..	..	85 "
Sulphur dioxide gas	..	..	..	..	65 "
Hydrogen sulphide gas	..	..	..	..	55 "
Carbon dioxide gas	..	..	..	..	35 "
Oxygen gas	..	..	..	..	9.25 "

(See Colloid Chemistry (Adsorption).)

**Carbon Black** — See same.

Certain **activated carbons** are made by subjecting carbonaceous matters (such as nut-shells) of high density and stone-cell structure to a process of distillation at above 700° C., and then submitting the residual product to the action of steam whilst still hot, or that of other oxidizing gas. This treatment, without causing appreciable combustion of the carbon, removes hydrocarbons, which are said to render the carbon inert. As thus prepared, it is used in gas masks ; for clarifying and decolorizing liquids ; in benzol recovery plants for the extraction of hydrogen sulphide from coal and coke-oven gases ; the production of sulphur dichloride ; the removal of fusel oil from alcohol ; for assisting in the production of high vacua ; in the removal of odour from water ; the removal of disagreeable fumes from various processes, and the recovery of vapours. Activated carbon that has been used can be revived by subjecting it to the action of steam at regulated high temperature. This treatment serves in some cases the purpose also of recovering a desired adsorbed material.

The amount of adsorption on various grades of carbon depends upon (1) the kind of material from which the carbon is prepared, (2) the method of preparation, in which the temperature to which the material is subjected is a controlling factor, and also the removal of residual gases, as by subjecting the resulting carbon to the action of steam, (3) the kind of material to be adsorbed, and (4) the temperature during adsorption. Dewar (1906) showed that 5 grams of coconut charcoal at the temperature of liquid air reduced the pressure of air in a one-litre container from 1.7 mm. to 0.00005 mm. This has since become the basis for the production of high vacua. When the adsorbed material is a gas, a fifth criterion is the pressure, as shown by Freundlich.

The commercial methods of activating carbon have been summed up as follows :

1. By heating *in vacuo* at from 300° to 1,200° C.
2. By exposing to superheated steam at from 300° to 800° C.
3. By heating in contact with reducing gases at from 500° to 800° C.
4. By combining the methods (2) and (3).
5. By treatment with solutions of certain salts, then reheating, washing, and purifying the resultant carbon.

There is, however, no one type of activated carbon that is universally and equally effective for all purposes. It would appear that oxygen may be adsorbed on a charcoal surface forming three types of surface compounds—one removable only as oxides of carbon at extremely high temperatures; another removable as oxides by evacuation or by fusion with sodium carbonate; and the third formed in larger quantities by adsorption at low temperatures recoverable as oxygen.

**References:** "A Resumé on Active Carbon and Its Industrial Applications" in *Chem. and Ind.*, **29**, 3 (1933); "Adsorption of Solvent Vapors on Commercial Activated Carbon," by Sawyer and Othmer (*Ind. Eng. Chem.*, **36**, 894 (1944)); *Industrial Carbon*, by C. L. Mantell (D. Van Nostrand, New York); Bone Black, Charcoal, and Lamp Black.

**Thermatomic Carbon** — See Carbon Black.

**Vegetable Matters** — There is an immense number of vegetable organic products, many of which can be built up artificially by synthetic processes. Amongst these substances may be mentioned formaldehyde, urea, alcohol, glycerol, tartaric acid, indigotine, vanillin, alizarin, coumarin (the odoriferous principle of the Tonka bean) and many perfumes. (See Plant Life.) We may well wonder at the marvellous extent and nature of the structures, tissues, colouring matters, and other products that characterize vegetable life, built up out of the constituents of the soil and the air by the living agencies contained in their seeds. They find their parallel in the animal kingdom, and in the wonderful determining force that causes many salts in a state of solution to crystallize out therefrom in beautiful geometrical forms. (See Crystals.)

**Animal Matters** — Compounds of which carbon forms an important constituent are generally termed *organic*, and all of them are combustible—that is to say, they can be wholly or partially burned up if heated sufficiently in the presence of plenty of air or oxygen and leaving only the ash, consisting of mineral matters which were present before burning.

There are many **organic compounds** composed of carbon and hydrogen only, termed hydrocarbons, including such substances as methane or marsh-gas ( $\text{CH}_4$ ), acetylene ( $\text{C}_2\text{H}_2$ ), benzene ( $\text{C}_6\text{H}_6$ ), naphthalene ( $\text{C}_{10}\text{H}_8$ ), and turpentine ( $\text{C}_{10}\text{H}_{16}$ ). (See Hydrocarbons.)

Cyanogen ( $\text{C}_2\text{N}_2$ ) consists of carbon and nitrogen only.

Many others contain oxygen in addition to carbon and hydrogen, alcohol ( $\text{C}_2\text{H}_6\text{O}$ ), glycerol ( $\text{C}_3\text{H}_8\text{O}_3$ ), acetic acid ( $\text{C}_2\text{H}_4\text{O}_2$ ), phenol ( $\text{C}_6\text{H}_6\text{O}$ ), the carbohydrates, and the fats being instances of this class.

Another class consists of carbon, hydrogen, and nitrogen, including prussic or hydrocyanic acid ( $\text{HCN}$ ) and aniline ( $\text{C}_6\text{H}_7\text{N}$ ) (see Amines); and further groups containing oxygen in addition to these three elements, such as urea ( $\text{CH}_4\text{ON}_2$ ), indican ( $\text{C}_{14}\text{H}_{17}\text{O}_6\text{N}$ ), morphine ( $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$ ), and quinine ( $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$ ).

There are still more complicated organic substances in which other elements exist in combination with carbon, along with one or more of those already mentioned, such as sulphur, phosphorus, chlorine, bromine, and iodine.

Other organic compounds of very complex composition exist in the flesh, the brains, and other parts of living creatures, the chief solid parts of the living tissues of animals consisting of so-called albumins. (See Albumins.)

**CARBON BLACK**—Generically carbon black is a name that covers a large number of technologically useful carbon forms. Uses are found in the ink, paint, and rubber industries. The use of carbon black in ink and paints is very old, but the use of carbon blacks in rubber is recent. Stillwagon (*India Rubber World*, **96**, 39 (1937)) states it was first used in rubber by a company at Silvertown, England. Later, George Oenslager developed the carbon-black tread subsequent to the observation that 10 volumes of carbon per 100 volumes of rubber gave good results under abrasive service conditions. The carbon used in those experiments was made by the channel process, in which the luminous flame of burning natural gas comes in contact with a cold iron surface. Carbon is deposited, which is subsequently removed by a scraper.

The thermal decomposition and furnace type blacks were developed almost simultaneously. The thermal decomposition blacks are made by decomposing natural gas on highly heated (2,400–2,600° F.) siliceous brick, the resulting carbon being later filtered from the gaseous products of decomposition by bag filters.

The furnace-type blacks are made in a furnace reminiscent of the lampblack furnaces. The gas, sometimes enriched with liquid hydrocarbon vapours, is burned under incomplete combustion conditions, and the products, after cooling, are separated by cyclones.

#### CARBON BLACKS FOR RUBBER

Symbol *	Name	Type	Use
H.P.C.	Hard Processing Channel	Channel	Tyres
M.P.C.	Medium Processing Channel	"	"
E.P.C.	Easy Processing Channel	"	"
C.C.	Conducting Channel	"	"
H.A.F.	High Abrasion Furnace	Furnace	Mechanical†, Tyres
H.M.F.	High Modulus Furnace	"	"
S.R.F.	Semi Reinforcing Furnace	"	"
R.F.	Reinforcing Furnace	"	"
C.F.	Conducting Furnace	"	"
F.F.	Fine Furnace	"	"
V.F.F.	Very Fine Furnace	"	"
F.E.F.	Fast Extruding Furnace	"	"
F.T.	Fine Thermal	Thermal Decomp	"
M.T.	Medium Thermal	"	Tubes, Mechanical
—	Lampblack	Furnace	Mechanical

\* *Rubber Red Book*, 1949 (Rubber Age, Palmerton Publishing Company, New York).

† Mechanical refers to such rubber goods as hose, belting, shoe heels, battery cases, and automotive parts other than tyres and tubes.

D. Parkinson (*Rubber Chem. Tech.*, **17**, 451 (1944)) presents some comparisons of particle size and area with various properties in the finished article :

Symbol	Name	Mean Diameter m $\mu$	Specific Surface sq. cm. $\times 10^4$ per g.
M.T.	Thermax	274	10
—	Lampblack	97	23
S.R.F.	Gastex, Furnex	82-3	31
F.T.	P-33	74	36.5
C.F.	Acetylene black (Shawinigan)	43	65
H.P.C.	Dixie	41	63
V.F.F.	Statex	34	75
—	Spheron-9	30	86
H.P.C.	Spheron-4	28	94.5
C.C.	Spheron-1	24	107
—	Super Spectra	13	198

Resiliency, abrasion resistance, and colour are inversely proportional to the particle size.

*References*: Carbon Black, Activity, *Rubber Chem. and Tech.*, **13**, 437 (1940); Adsorption, *Ind. and Eng. Chem.*, **23**, 646 (1931); Adsorptive Properties, *India Rubber Jour.*, **88**, No. 16, 457 (1934); Conductivity in Treads, *Ind. and Eng. Chem.*, **35**, 806 (1943); Dielectric Effect in Rubber, *Rubber Chem. and Tech.*, **12**, 317 (1939); Effect of Diameter and Surface Area, *Rubber Chem. and Tech.*, **17**, 451 (1944); Effect of Diameter and Surface Area in GR-S, *Trans. Inst. Rubber Ind.*, **21**, No. 1, 7 (1945); Effect of Grit, *Rubber Age (N.Y.)*, **29**, No. 2 (1931); Effect on Physical Properties of Rubber, *Ind. and Eng. Chem.*, **20**, 817 (1928); Identification by Surface Area, *Ind. and Eng. Chem., Anal. Ed.*, **15**, 256 (1943); Moisture Content, *Rubber Age (N.Y.)*, **26**, No. 9 (1930); Particle Size and Shape, *Rubber Chem. and Tech.*, **14**, 52 (1941), **15**, 657, 664 (1942); *Kautschuk*, **17**, No. 1, 1 (1941); *Rubber Chem. and Tech.*, **14**, 920 (1941); Properties, *Trans. Inst. Rubber Ind.*, **5**, No. 4, 263 (1929); pH Properties, *Ind. and Eng. Chem.*, **29**, 953 (1937); Role of Oxygen, *Ind. and Eng. Chem.*, **21**, 1288 (1929); Surface Chemistry, *Ind. and Eng. Chem.*, **27**, 571 (1935); Volatile Constituents, *Ind. and Eng. Chem.*, **20**, 904 (1928).

**CARBON DIOXIDE** — See Carbon Oxides.

**CARBON DISULPHIDE** (CS<sub>2</sub>) as ordinarily made is an evil-smelling heavy, mobile, poisonous, and highly inflammable liquid, which may be prepared by passing the vapour of sulphur over red-hot carbon, the volatile product being condensed in properly cooled vessels. It is made industrially in a carbon-arc electric furnace from coke and sulphur. Carbon disulphide can be obtained in practically odourless or pleasantly smelling form by first shaking up with mercury, and after separation, allowed to stand for a short time in presence of 2 per cent. pure fat, followed by distillation. It is a colourless, highly refracting

liquid which, when pure, boils at  $46.3^{\circ}\text{C}$ ., freezes at  $-109^{\circ}\text{C}$ . into tetragonal crystals, has a sp. gr. of 1.261, and is soluble in water to the extent of 0.258 g. at  $0^{\circ}\text{C}$ . and 0.195 g. at  $30^{\circ}\text{C}$ . per 100 g. of water.

Carbon disulphide is manufactured on a considerable scale, and employed in the manufacture of viscose, also as an insecticide, a solvent of caoutchouc and fats, and in processes of extraction of essential oils and perfumes. It yields a vapour of great insecticidal power in respect of ants, white grubs, mole crickets, moths, and other pests including those which affect stored corn; an atmosphere composed of 1 part vapour and 90 parts of air being fatal to most insects. As applied for Phylloxera treatment, the liquid is introduced into the soil some depth below the surface, so that it slowly volatilizes, the vapour thus reaching the pests against which it is applied in a diffused manner. It is usual to apply about 10 ounces per vine, using half that quantity (150 grams) in each of two applications ten or twelve days apart. Miscible emulsions of it are also used for destroying the Japanese beetle in the soil without damaging the plants, one such emulsion being made from the disulphide, castor oil, potassium hydroxide, denatured alcohol and water.

**CARBON ELECTRODES**, as used for electric furnace work, are of several kinds, being variously made of graphite, coke, charcoal, lamp-black, and anthracite coal; others of carbon derived from the baking of coal-tar pitch of m.p. from  $150^{\circ}$  to  $200^{\circ}\text{F}$ . A good pitch of this character loses nearly all its volatile matter at  $600^{\circ}\text{F}$ . The electrodes are formed by working up the cleaned powdered material, such as coke with tar or pitch, then pressing to the desired shape by ramming the material into moulds, wherein it is calcined in a gas-fired kiln at about  $1,100^{\circ}\text{C}$ ., with the exclusion of air. For carbide furnaces, electrodes up to 3 m. long and of 80 cm. diameter, weighing about 2 tons, capable of carrying 8,000 kw., are used in furnaces yielding 50 tons of product per day; while for use as anodes in making aluminium the electrodes must be of great purity, giving less than 1 per cent. ash. Acheson graphite is stated to be most suitable for anodes to be used in the electrolytic manufacture of chlorine and caustic soda by the porous diaphragm process.

**CARBON MONOXIDE** — See Carbon Oxides, and Poisons.

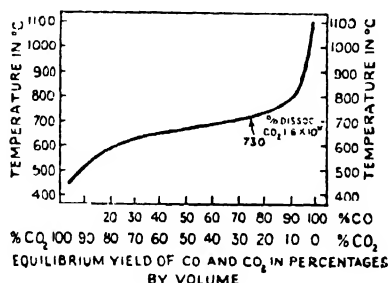
**CARBON OXIDES** — **Carbon monoxide gas** (CO) is the principal product when carbon is burned at a bright red heat. It is also produced whenever carbon is burned with an insufficient supply of oxygen to convert it into the dioxide, and may be prepared by passing a stream of carbon dioxide gas over charcoal heated to redness ( $\text{CO}_2 + \text{C} = 2\text{CO}$ ), and in pure form by heating formic acid with strong sulphuric acid ( $\text{H.COOH} = \text{CO} + \text{H}_2\text{O}$ ). It suffers catalytic dissociation at temperatures varying with the nature of the catalyst,  $400^{\circ}\text{C}$ . being necessary when glass forms the only contact surface. Its decomposition in the silent electric discharge has been studied by Lunt and Mumford, and W. A. Bone has summarized the results of fifty years' experimental research on the influence of steam on the combustion of carbonic oxide in his *Liversidge Lecture of 1930 in J. Chem. Soc., 1931, 338*. It has been

demonstrated that a dry mixture of carbon monoxide and oxygen can be made to combine with explosive violence by a sufficiently powerful electrical condenser charge.

Carbon monoxide is colourless, poisonous, of m.p.  $-211^{\circ}\text{C}.$ ; slightly soluble in water, 1 volume of which at  $0^{\circ}\text{C}.$  dissolves 0.0328 volume, and is utilized in a process for the manufacture of the metal nickel. It often occurs at times in coal mines, and is known as *white-damp*. A rescue apparatus for use in cases of carbon monoxide poisoning

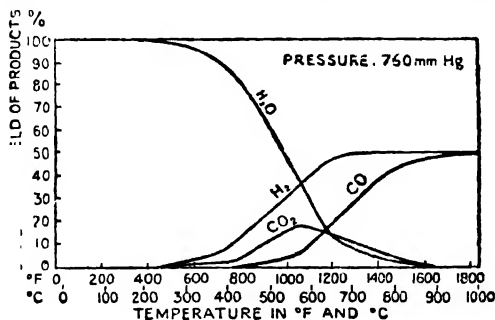
### $\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}$ REACTION

#### EQUILIBRIUM CONCENTRATION—TEMPERATURE RELATIONSHIP



### $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$ REACTION

#### EQUILIBRIUM CONCENTRATION—TEMPERATURE RELATIONSHIP



depends for its efficacy upon the use of so-called "*Carbogen*"—that is, a mixture of oxygen with 5 per cent. of carbon dioxide. (See "*Carbon Monoxide as a Raw Material for Chemical Synthesis*," by N. W. Krase, *Transactions of the American Institute of Chemical Engineers*, **32**, 493 (1936); *Textbook of Inorganic Chemistry*, by J. N. Friend, Vol. 5, Carbon and Its Allies (article on Carbon Monoxide) (C. Griffin and Co., London); *Acetylene and Carbon Monoxide Chemistry*, by John W. Copenhaver and M. H. Bigelow (Reinhold Publishing Corp., New York); *Gas (Coal), Nickel, Oxo Process, "Synthol," and Water Gas.*)

**Carbon Dioxide** ( $\text{CO}_2$ ) is the colourless gaseous product obtained whenever carbon or a carbon-containing substance is burned with a sufficiency of oxygen, and admits of condensation into the liquid and solid forms. It is exhaled from the animal body in the process of respiration, the carbon dioxide being the product of oxidation of carbon of food. It is one of the constituents of what is called *black-damp* or *choke-damp* by coal-miners, and often occasions loss of life in mines after explosions. It can readily be produced by the action of acids upon carbonates, such as calcium carbonate (chalk and marble), and when hydrochloric acid is used in this process the change that takes place is represented as follows:  $\text{CaCO}_3 + 2\text{HCl} = \text{CaCl}_2 + \text{H}_2\text{O} + \text{CO}_2$ —carbon dioxide gas escapes in a brisk effervescence, calcium chloride being left behind in

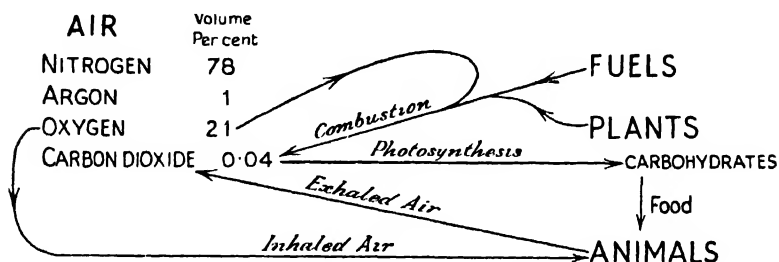


Diagram Showing Selected Relationships of Carbon Dioxide.

solution. There is also a cheap method for its production based upon the reaction between sodium bicarbonate and sodium bisulphate.

In solid form known as "Dry Ice" it is now made on a large scale from the liquefied substance by a process of which there are several modifications. In one of these, the liquid is cooled in coils by which it is raised to the top of a chamber in which the pressure is lowered to 6.2 atm. by expansion across an orifice; the resultant mixture of liquid and solid carbon dioxide is then thrown on to a filter at the floor of the chamber from which the liquid is subsequently removed, leaving in due course a solid block of the "dry ice." It is also made by the "Backhouse" process by the adiabatic expansion of the cooled liquefied substance. The gas is expanded to a pressure of 15 lbs. per sq. in.; from 50 to 60 per cent. evaporates and is subsequently returned; while the remainder solidifies and is then moulded and pressed into blocks. These are packed in wooden cases and the article constitutes a stable product which can be sold at half the price of the liquefied form, being used for preserving perishable goods and, among other applications, for refrigerating cars making long journeys, 1 part replacing 15 parts of water and 3 parts of salt.

One volume of water at  $0^\circ\text{C}$ . dissolves 1.713 volumes of carbon dioxide (or 19.75 lbs. per 1,000 gallons of water), which is employed commercially in many ways both as gas and in liquefied forms; amongst other applications, for impregnating water under pressure, making what is called "soda-water," and as a fire extinguisher. Its melting

point is  $-56.6^{\circ}\text{C}$ . at 5.2 atm. pressure, and it sublimates at  $-78.5^{\circ}\text{C}$ . Liquid carbon dioxide is shipped in high-pressure steel cylinders, and is used as a fire extinguisher. Besides the well-known alkalis, amines and alcohol-amines are utilized for the absorption of carbon dioxide. The addition of a reagent, such as soap or formaldehyde, that lowers the surface tension of the absorbing liquid is advantageous.

It is sometimes met with in liquid globule form in certain minerals, and is elsewhere referred to as a constant gaseous constituent of the atmosphere (3 to 4 parts per 10,000 parts air). (See *Carbon Dioxide*, by E. L. Quinn and C. L. Jones (Reinhold Publishing Corp., New York); Air, Photocatalysis, Plant Life, and Refrigeration.)

**Carbonic Acid** ( $\text{H}_2\text{CO}_3$ ) — This combination of carbon dioxide with water, although itself an unstable body, forms with bases a great series of well-defined compounds known as carbonates. (See Carbonates.)

There are several percarbonates, including the true ones (analogues of the persulphates), the potassium and sodium perdicarbonates being obtained by electrolysis of cold saturated solutions of the normal carbonates, or by the action of carbon dioxide on the peroxides in presence of absolute alcohol. In common with sodium perborate and the persulphates they are used as bleaching and oxidizing agents.

**Carbon Suboxide** ( $\text{C}_3\text{O}_2$ ) is a gas obtained by dehydrating malonic acid or in a yield of 41 per cent. by pyrolysis of diacetyltartaric anhydride (Hurd and Pilgrini, 1933). It is possibly of the structure  $\text{O} : \text{C} : \text{C} : \text{C} : \text{O}$ . The boiling point is  $7^{\circ}\text{C}$ .

**CARBON TETRACHLORIDE** (Tetrachloromethane) ( $\text{CCl}_4$ ) — A thin, colourless, poisonous liquid, of pungent aromatic odour, b.p.  $76.8^{\circ}\text{C}$ ., prepared from carbon disulphide by the action of chlorine. It has a sp. gr. of 1.595, freezes at  $-22.6^{\circ}\text{C}$ ., and is largely used as a solvent for fats, in fire extinguishers, as a drug in cases of hook-worm, as a parasiticide, and in making cleansing compounds. Experience has shown that it is dangerous to use carbon tetrachloride fire extinguishers in confined spaces where users cannot avoid breathing the poisonous fumes (containing phosgene) that are produced by its decomposition; moreover, it is not without action on the metal parts of chemical plant, particularly in presence of moisture, owing to the production of hydrochloric acid. (See Solvents.)

**CARBON TRICHLORIDE** — See Hexachloroethane.

**CARBONATES** — Compounds containing the radical  $\text{>CO}_3$  combined with a metallic ion or radical or with an organic (usually alkyl) radical. The common soluble carbonates are sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), potassium carbonate ( $\text{K}_2\text{CO}_3$ ), and ammonium carbonate ( $(\text{NH}_4)_2\text{CO}_3$ ). The remaining common carbonates are relatively insoluble. Bicarbonates are soluble, for example, sodium bicarbonate ( $\text{NaHCO}_3$ ), and calcium bicarbonate ( $\text{Ca}(\text{HCO}_3)_2$ ). Insoluble carbonates are readily prepared by precipitation of a salt solution of the metal in question with a soluble carbonate solution, followed by separation of the resulting precipitate, usually by filtration.

## DISSOCIATION PRESSURES AND TEMPERATURES OF CARBONATES

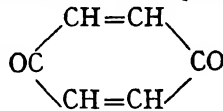
Carbonate	Dissociation Pressure mm. Hg.	Corresponding Temperature °C.
$\text{Li}_2\text{CO}_3$	50	880
$\text{Na}_2\text{CO}_3$	50	1,220
$\text{K}_2\text{CO}_3$	50	1,150
$\text{Rb}_2\text{CO}_3$	50	1,150
$\text{Cs}_2\text{CO}_3$	50	1,050
$\text{MgCO}_3$	760	230
$\text{CaCO}_3$	760	820
$\text{SrCO}_3$	760	1,130
$\text{BaCO}_3$	760	1,300
$\text{FeCO}_3$	760	400
$\text{MnCO}_3$	760	330
$\text{PbCO}_3$	760	350
$\text{Ag}_2\text{CO}_3$	760	275

See Carbon Oxides (Carbonic Acid).

**CARBONIFEROUS** — The oldest or Palæozoic system of geological formation, including the coal measures.

**CARBONIZATION** — See Coal.

**CARBONYL** — The group,  $\text{:C:O}$ , which is characteristic of aldehydes

$\left(\frac{\text{H}}{\text{R}} > \text{CO}\right)$  and ketones  $\left(\frac{\text{R}}{\text{R}} > \text{CO}\right)$ , and of quinones .

(See Metallic Carbonyls, and Nickel.)

**CARBONYL CHLORIDE (Phosgene)** ( $\text{COCl}_2$ ) is formed when a mixture of carbon monoxide and chlorine gases in equal volumes is exposed to sunlight, and was used for "gassing" in World War I, being a suffocating and extremely poisonous gas. It is produced by passing a rapid current of the mixed gases, at the ordinary temperature, over highly activated wood charcoal, the product being liquefied by use of a freezing mixture. The liquefied carbonyl chloride, of sp. gr. 1.39 and b.p.  $8.2^\circ \text{C}$ ., immediately assumes the gaseous form upon exposure to the air. Petrol, benzol, and ethyl acetate dissolve an equal weight of the gas, and these solutions are used in the coal-tar colour industry, also for exterminating rats and moles, for making synthetic essence of violets, and for removing iron oxide from certain glasses so as to increase their refractiveness.

**CARBONYL FERROCYANIDES** as found in spent oxide of iron and in "cyanogen mud" products (obtained in the purification of coal gas) can be easily recovered from the crude mother-liquor resulting from the production of potassium and sodium ferrocyanide from these materials, and have been found useful as oxygen carriers in dyeing and printing processes. Sodium carbonyl ferrocyanide has also proved useful as a substitute for prussiate in making aniline blacks.

**CARBONYL SULPHIDE** (O : C : S) — A colourless gas, of boiling point  $-50^{\circ}\text{C}$ .

**"CARBORAFFIN"** — A carbonaceous decolorant black, made by mixing peat with a strong solution of zinc chloride, drying, and heating to  $700^{\circ}\text{F}$ ., and then washing with dilute hydrochloric acid and water. This is stated by Stanek to have 80 times the decolorizing power of bone char.

**"CARBORUNDUM"** — See Abrasives.

**"CARBOSIL"** — A proprietary water-softening material, being a combination of sodium carbonate and silicate, used also as a detergent.

**"CARBOWAXES"** — A proprietary name for solid polymers of ethylene glycol, having the general formula  $(\text{CH}_2\text{OH} \cdot (\text{CH}_2 \cdot \text{O} \cdot \text{CH}_2)_n \cdot \text{CH}_2\text{OH})$ . The carbowaxes are available commercially in various grades each consisting of a mixture of several polymers. "Carbowax" 1500 is a semi-solid wax, having a consistency and appearance similar to that of white soft paraffin. "Carbowax" 1540 is a solid wax, melting at about  $40^{\circ}\text{C}$ . and approximating in appearance to hard paraffin. The member graded as 4000 is a solid wax issued in the form of flakes melting between  $50^{\circ}$  and  $55^{\circ}\text{C}$ . The "Carbowax" compounds are completely soluble in water but are immiscible with vegetable and mineral oils; they will themselves dissolve many organic compounds, notably the sulphonamides. Methods of synthesis of the higher polymers of ethylene glycol are described by Perry and Hibbert in *Canad. J. Res.*, **A14**, 77 (1936). The "Carbowax" compounds have found various industrial uses and have been used in the formulation of cosmetic preparations and ointment bases. Their use in ointment bases is described by Niemeyer in *J. Amer. Pharm. Ass.*, (Prac. Ed.) **8**, 194 (1947) and by Hadgraft and Brain in *Lancet*, **2**, 78 (1949) (see also Hopkins in *J. Invest. Derm.*, **7**, 4 (1946)).

**"CARBOXIDE"** (UCC)—Trade-mark for a mixture of ethylene oxide and carbon dioxide used as fumigant, fungicide, germicide, and insecticide.

**CARBOXYL GROUP**  $\left( \begin{array}{c} -\text{C}=\text{O} \\ | \end{array} \right)$  — Characteristic of the monobasic fatty

and other organic acids, the H of which is replaced in the formation of salts and esters.

**CARBOXYLIC ACIDS** — Organic acids that contain the carboxyl group. (See Acids.)

**CARBROMAL** ("Adalin") ( $\text{C}_7\text{H}_{13}\text{O}_2\text{N}_2\text{Br}$ ) — A white crystalline substance, namely,  $\alpha$ -bromo- $\alpha$ -ethylbutyrylcarbamide,  $\text{CBr}(\text{C}_2\text{H}_5)_2\text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ ; sparingly soluble in water; soluble in alcohol, ether, and chloroform; m.p.  $116^{\circ}$  to  $118^{\circ}\text{C}$ . Used in medicine as a mild sedative and hypnotic.

**CARBUNCLE** — See Garnet.

**CARBURETTED WATER GAS** — See Water Gas.

**"CARBURITE"** — A smokeless fuel produced by a special process of carbonizing coal.

**CARDAMOMS** — The dried, nearly ripe fruits of *Elettaria Cardamomum* var. *minuscula*, a shrub which is cultivated on the Malabar coast and islands in the Indian sea ; used as a condiment and stimulant aromatic. They yield from 3 to 8 per cent. of volatile oil of sp. gr. from 0.923 to 0.945 at 15° C., optical rotation 20° to 44°, and ref. ind. 1.461 to 1.467 at 20° C., according to the kind, there being several oils on the market, known as Ceylon, Malabar, Siam, etc. Oils derived from other species are inferior in quality. Old cardamom oil has been found to deposit crystals of a terpene hydrate,  $C_{10}H_{16}, 3H_2O$ . Cardamom oil contains cineole, terpineol, and limonene in combination with formic and acetic acids, and is used in medicine as a flavouring agent and carminative.

**"CARDIAZOL"** — See Leptazol.

**"CARDOPHYLLIN"** — See Aminophylline.

**CARENE** — See Sylvestrene.

**CARMINE** — See Cochineal.

**CARMINIC ACID** — See Cochineal.

**CARNALLITE** — An important constituent ( $KCl.MgCl_2.6H_2O$ ) in natural brines and salt beds in Stassfurt, Germany. It has been an important source of raw material for the electrolytic production of magnesium metal (see Magnesium). The Stassfurt salts contain about 0.02 per cent. of rubidium chloride and 0.0002 per cent. of caesium chloride. (See Potassium.)

**CARNAUBA WAX (Brazil Wax)** — See Waxes.

**CARNELIANS** — See Cornelians.

**CARNOTITE** — Mineral uranium potassium vanadate of yellowish colour and variable composition. (See Radium, Uranium, and Vanadium.)

**CARO'S ACID (Permonosulphuric Acid)** ( $HO.SO_2.O.OH$ ) — A white crystalline solid, of m.p. about 45° C.; relatively stable; a strong oxidizing agent, liberating iodine from potassium iodide immediately, oxidizing ferrous salts to ferric, sulphur dioxide to sulphur trioxide, hydrogen chloride to chlorine, but not reactive with permanganate, chromate, nor titanium salts (distinction from hydrogen peroxide). Made by the reaction of concentrated sulphuric acid and hydrogen peroxide.

**CAROA FIBRE** (*Neoglazoria variegata* of Brazil) — Suggested for employment in paper-making and the textile industry.

**CAROB** — See Locust Kernel.

**CARONE** ( $C_{10}H_{16}O$ ) — A cyclic ketone of the terpene series, being a colourless oil; b.p. 210° C., with an odour of peppermint and camphor.

**CAROTENE** — See Carotinoids, and Plant Colouring Matters.

**CAROTINOIDS (Carotenoids)** — A group of naturally occurring, fat-soluble pigments, of which more than sixty are now known. The most ubiquitous are carotene and xanthophyll which occur associated with chlorophyll in the chloroplasts of plants. Lycopene is the pigment

responsible for the red colour of the tomato, while fucoxanthin and rhodoxanthin are respectively the predominating pigments of the brown and red algæ. (See Plant Colouring Matters.)  $\beta$ -carotene has assumed great importance since it has been shown to be the precursor of Vitamin A, into which it is converted in the liver. (See F. Mayer, *The Chemistry of Natural Coloring Matters* (Reinhold Publishing Corp., New York); P. Karrer and E. Jucker, *Carotenoids* (Elsevier Publishing Co., New York and London); Chlorophyll, Plant Colouring Matters, and Vitamins.)

**CARRAGEEN** — See Sea-weeds.

**CARRIER ELEMENT** — See Nuclear Chemistry.

**CARRON OIL** — A mixture of equal parts of linseed oil and lime-water, formerly a popular domestic remedy for application to burns.

**CARTHAMUS** — See Safflower.

**CARVENE** — A terpene ( $C_{10}H_{16}$ ) contained in oil of cumín.

**CARVONE (Carvol)** ( $C_{10}H_{14}O$ ) — The principal constituent of oil of caraway and dill seeds; a colourless, liquid ketone isomeric with thymol; used in medicine in the above oils as an aromatic and carminative, and pure as an anthelmintic; sp. gr. 0.960, and b.p.  $225^{\circ}C$ . (See Caraway Oil.)

**CASCARA SAGRADA (Persian Bark, Sacred Bark)** — The dried bark of *Rhamnus Purshiana* (Fam. Rhamnaceæ), a species of buckthorn indigenous to British Columbia and several Western States of the U.S.A. It contains emodin, a derivative of hydroxymethylanthraquinone, and an unidentified purgative principle. It is used in medicine, in the form of its extracts, as a laxative.

**CASCARILLA BARK** — The dried bark of shrubs (*Croton eleutheria* and *Croton cascarrilla*) indigenous in the West Indies and Bahama Islands. In addition to other extractives, it yields from 1.5 to 2 per cent. of a volatile aromatic oil and a crystalline bitter principle, cascarrillin. The bark infusion is used medicinally as a cathartic, stomachic, tonic, and expectorant.

**CASE-HARDENED STEEL** — See Iron.

**CASEIN**, the nitrogenous constituent of the milk of mammalia, is a member of the group of proteins, somewhat allied to legumin or vegetable casein, and has colloidal properties. Cow's skimmed milk is the principal source of the commercial article, and contains from 2.5 to 4.2 per cent. Curdling is generally effected by the addition of very dilute hydrochloric, sulphuric, or acetic acid, or rennet, and the curd thus produced and sometimes further purified is washed and dried. The yield of casein by the natural souring method resulting from the production of lactic acid is usually less than that of the other methods. The English casein, as prepared by precipitation with acid, is also known as "caseinogen." Soya beans constitute another valuable source, the casein being extracted from the beans when freed from oil, by digestion with a 5 per cent. solution of sodium carbonate, followed by precipitation with a 5 per cent. solution of hydrochloric acid.

Casein is white to yellowish in colour, insoluble in water, but soluble in alkaline solutions, the soluble form as sold being casein, to which some proportion of sodium borate (about 10 per cent.) or sodium carbonate (about 20 per cent.) has been added. Its composition may be approximately expressed as follows: carbon, 53·8 per cent.; hydrogen, 7·2 per cent.; nitrogen, 15·6 per cent.; oxygen, 22·5 per cent. and sulphur, 0·9 per cent.

It finds commercial applications in the sizing and dressing of cotton, as a silk weighting agent, and particularly as a binding material in the compounding of distempers and other water paints capable of giving surfaces little affected by rain. (See Lime Washes.) It is also used in the preparation of foods, plastics, ivory substitutes, insecticides, and for coating paper, etc. Its value as an adhesive is referred to under Adhesives. Good rennet-made casein is the only sort fit for use in making plastics in imitation of tortoiseshell, jade, lapis lazuli, brush-backs, buttons, etc. It is prepared by moistening with 25 per cent. water, in which it swells, and is then forced into the shape of rods, and subsequently rolled out in sheet form and put in a bath of 10 per cent. formaldehyde, which penetrates and prevents the sheet, when dried, from further loss of water.

Calcium caseinate is used medicinally.

*References:* *Casein*, by E. L. Tague (Constable and Co., London); *Casein and Its Industrial Applications*, by E. Sutermeister and F. L. Browne (Reinhold Publishing Corp., New York); Adhesives, Cheese, "Galilith," "Lanital," Milk, and Paints.

**CASHEW-NUT OIL** — A pale, non-drying yellow oil expressed from the kernels of the fruit of *Anacardium occidentale*, N.O. Terebinthaceæ (widely distributed in tropical regions, including the E. and W. Indies, South America, India, and the Pahang district of the Malay Peninsula); the yield being from 40 to 45 per cent. It requires high pressure for extraction, and the cake remaining after crushing of the oil is rich in albuminoids. The oil is stated to consist mainly of anacardic acid and cardol, and is soluble in alcohol, ether, etc.; sap. v. about 180, i.v. 60·6; used in medicine; also for colouring oils and fats. The nuts are used for icing almonds.

**CASING-HEAD GAS** — See Petroleum.

**CASSAVA** — The West Indian name of a starch obtained from the roots of the *Manioc* (*Jatropha manihot* L.), growing in the East and West Indies, from which tapioca, laundry starches, and power alcohol are made. Manioc is the Brazilian name for the product of *Manihot utilisima*, cultivated largely in S. America. (See Manioc, and Tapioca.)

**CASSIA BARK** (Chinese Cinnamon) — The bark of *Cinnamomum Cassia* (Fam. Lauraceæ), an evergreen tree growing in China and cultivated in other parts of Eastern Asia. It yields, on distillation, from 1 to 2 per cent. of volatile oil which contains about 80 per cent. of cinnamic aldehyde and resembles cinnamon oil but is inferior as a flavouring agent. Cassia buds consist of the unripe fruits of *Cinnamomum*

*Loureirii* and possibly other species of *Cinnamomum*; they contain about 1·6 per cent. of volatile oil which is less pleasantly aromatic than cassia oil and is used in perfumery, as a flavouring agent and as a source of cinnamic alcohol. (See Cinnamon, and Cinnamyl Alcohol.)

**CASSIA FRUIT (Cassia Pod)**—The ripe fruits of *Cassia fistula* (Fam. Leguminosæ), a tree growing in India. It contains mucilage, pectin, and derivatives of hydroxymethylanthraquinone; the aqueous extract of the fruit is used in medicine as a laxative.

**CASSIA OIL**—A volatile oil obtained from the leaves and twigs of *Cinnamomum Cassia*, containing about 80 per cent. of cinnamic aldehyde together with cinnamyl acetate and a terpene; sp. gr. 1·055 to 1·065, ref. ind. 1·600 to 1·606 at 20° C.; used as a flavouring agent and in medicine as a carminative.

**CASSITERITE** ( $\text{SnO}_2$ )—The mineral otherwise known as *Tinstone*, of crystal system No. 2, and sp. gr. 6·4 to 7·1. It is found principally in Malaya, Indonesia, and Bolivia, also in Cornwall. (See Tin.)

**CASTANHA OIL (Brazil-Nut Oil)** is expressed from Brazil nuts, has a sp. gr. 0·918, sap. v. 193·5 and i.v. 106. It is pale yellow in colour, melts at 0·4° C., is soluble in ether and carbon disulphide, and used as an illuminant, in soap-making, perfumery, and as a food.

**CASTELIN**—See Glycosides.

**CASTILE SOAP**—See Soaps.

**CASTOR OIL**—A thick, non-drying, yellowish or pale green, odourless oil, extracted or expressed from the seeds of *Ricinus communis*, a plant indigenous in India and cultivated in Brazil, the East and West Indies, Java, Mexico, Panama, Manchuria, and other warm climates. The area under this seed in India is reported as about 1,250,000 acres. A mixture of several glycerides, upon saponification it yields a soap which is perfectly dissolved by water. Its chief constituent fatty acid is ricinoleic acid ( $\text{C}_{18}\text{H}_{34}\text{O}_2$ ) (contained in the form of triricinolein), and Heiduschka and Kirsten give the percentage composition of the oil as: ricinoleic acid 82, linoleic acid 1·4, oleic acid 6·8, dihydroxystearic acid (m.p. 142·5° C.) 1·3, stearic acid 3·4, glyceryl residue ( $\text{C}_3\text{H}_5$ ) 4·1, and unsaponifiable matter 0·3 per cent. The seeds of the plant yield from 45 to 55 per cent. oil, averaging 46·4 per cent. Medicinal oil is prepared from seeds which have been husked, while the second and third pressings are used industrially. The pressed cake is unfitted for cattle food, as it contains a poisonous body named "ricine," derived from the husks of the seeds. It is a good adhesive material for making plastics, and can be used, it is stated, in compounding tiles and bricks for interior building purposes.

Castor oil has a sp. gr. 0·958 to 0·969, acetyl value 183 to 186, ref. ind. 1·4695 to 1·4730 at 40° C., iodine value 82 to 86, solidification point  $-10^\circ$  to  $-18^\circ$  C., and is soluble in alcohol, ether, and benzene, but only slightly soluble in petroleum ether. The British Pharmacopœia restricts the free fatty acids in castor oil to a quantity not exceeding an acid value of 4, and it is to be noted that this content increases with ageing.

The bleaching of castor oil is usually effected by agitation at 200° F. with 2 to 4 per cent. of fuller's earth, followed by agitation with from 0.2 to 1.5 per cent. of prepared decolorizing carbon.

Castor oil is used in medicine and the lower qualities for soap-making, leather-dressing, as lubricants, in the preparation of Turkey-red oil, and in the manufacture of artificial leather, linoleum, and rubber substitutes. From it, also, several aldehydes can be prepared which are of strong odour and used in perfumery. Completely hydrogenated castor oil melts at 86° C., and has an iodine value 2. (See also Ricine, Ricinoleic Acid, and Turkey-red Oil.)

**CATALASE** — See *Aspergillus*, and *Enzymes*.

**CATALYSIS** — This term is used to describe all processes in which the rate of reaction is influenced, positively or negatively, by a substance called a catalyst which itself remains chemically unchanged at the completion of the reaction. Some examples of catalysis are: Conversion of starch into sugar by means of acid; decomposition of hydrogen peroxide in an alkaline solution; combination of hydrogen and oxygen in the presence of platinum to form water; the conversion of primary alcohols into aldehydes and hydrogen by passing their vapours through tubes containing certain metals or their oxides; the production of ethylene from ethyl alcohol by passing its vapours over silica or alumina at 280° C., the hydrogenation of oils using nickel catalyst; the synthesis of ammonia from its elements; the production of sulphur trioxide from sulphur dioxide and oxygen; and the catalytic cracking of petroleum.

If the rate of reaction is retarded by the catalyst it is said to be a *negative catalyst*. The term catalyst, when used alone, implies speeding up of reaction rates.

The following characteristics are exhibited by all catalysts:

(1) The amount of the catalyst at the finish of the process should be the same as at the beginning. It should be chemically unaffected although it may have undergone a physical change.

(2) A small amount of catalyst should cause large quantities of material to react. For example, one gram of colloidal platinum when present in a hundred million litres of hydrogen peroxide will catalyse its decomposition.

(3) Catalysts are usually specific for certain reactions. When reactants undergo several different reactions a catalyst may affect one reaction without affecting the others. For example, the catalytic cracking of petroleum for high-octane gasoline; alcohol vapour passed over alumina or kaolin yields ethylene and water, but if over finely divided nickel it yields acetaldehyde and hydrogen.

(4) The catalyst does not affect the amount of product made under a given set of conditions—it merely speeds up the rate at which the product is made. This is the same as saying that the point of equilibrium is not affected by the catalyst. A catalyst will affect both sides of a reversible reaction to the same degree.

The ability of a catalyst to initiate a chemical reaction is as yet unsettled in the minds of most authorities. There seems to be reliable evidence supporting two schools of thought, namely, those who contend that a reaction must be proceeding however slowly before a catalyst can have any effect, and those who cite the mutarotation of glucose and other related reactions whose mechanism seems to require the use of proton donors and acceptors which are in turn regenerated in the completed reaction.

For any reaction to occur there must be a decrease in free energy between the initial and final state. This is equivalent to saying there must be an inherent driving force present within the system in the desired direction. Whether or not the reaction is proceeding with a measurable rate will depend upon the necessary *energy of activation* required for the reaction mechanism which gives rise to the products. If the energy of activation is large the reaction will be proceeding with extreme slowness. The function of the catalyst is to bring about the desired reaction with a smaller energy of activation than that required by the uncatalyzed reaction mechanism. The catalyst may be likened to a guide taking travellers over a mountain (energy of activation) by utilizing the lowest mountain passes whereas, if left unguided, the travellers might take the highest peaks.

There are two main ways that a catalyst can by-pass the energy of activation requirement, namely, (1) the catalyst may form a complex with the reactants which then decompose into the products re-forming the catalyst, the whole process requiring less energy than the uncatalysed process; (2) the catalyst may act as a condensing surface upon which the reactants may be adsorbed, thus increasing their concentration and altering their energy content. In this way the catalyst could alter the reaction rate.

Foreign materials which tend to inhibit catalytic action are called *poisons*. Substances which tend to enhance the activity of catalysts are called *promoters*. When one of the products of a reaction acts as a catalyst for the reaction it is called an *autocatalyst*. For example, manganous ions catalyse the reaction of permanganates and oxalates in acid solution; oxides of nitrogen, produced in the reaction, catalyse the action of nitric acid and copper; the hydrolysis of an ester is catalysed by hydrogen ions whereby additional hydrogen ions are supplied as the reaction proceeds.

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*Catalysis* (2 volumes), edited by W. G. Frankenburg, V. I. Komarewsky, and E. K. Rideal (Academic Press, New York); *Twelfth Report of the Committee on Catalysis* of the National Research Council (John Wiley and Sons, New York, 1940); V. N. Ipatieff on *Catalytic Reactions at High Pressures and Temperatures* (Macmillan, New York); *Catalysis in Industrial Chemistry*, by Henderson (Longmans, Green and Co., London and New York); *Chemical Kinetics*, by Keith J. Laidler (McGraw-Hill Book Co., New York); Adsorption, Colloid Chemistry, Enzymes, Pressure (High), and Vitamins.

**CATALYTIC REACTOR** — A vessel charged with catalyst, in granular form or supported on trays, through which a liquid or gaseous mixture is passed in order to be subjected to a catalytic reaction. Such reactions usually take place at elevated temperatures, and the reaction mixture is preheated before entering the reactor. If the reaction is endothermic the vessel must be heated or insulated, if exothermic, it must be cooled. Catalytic reactors are used in the manufacture of sulphuric acid by the contact process, of ammonia by the Haber Process, in the catalytic cracking of petroleum oils, the hydrogenation and dehydrogenation of hydrocarbons, and the Fischer-Tropsch synthesis using hydrogen and carbon monoxide. For the design of catalytic reactors see R. Edgeworth Johnstone (*Trans. Inst. Chem. Engrs. (London)*, **17**, 129 (1939)); D. M. Hurt (*Ind. Eng. Chem.*, **35**, 522 (1943)); R. H. Dodd and K. M. Watson (*Trans. Am. Inst. Chem. Engrs.*, **42**, 263 (1946)); R. C. L. Bosworth (*Trans. Faraday Soc.*, **53**, 399 (1947)).

**CATAPHORESIS** — See Osmosis.

**CATECHOL** (*Ortho-dihydroxybenzene*) ( $C_6H_4(OH)_2$ ), known also as pyrocatechin and pyrocatechol, is a dihydroxy phenol of m.p.  $104^\circ C$ . and b.p.  $245^\circ C$ . found in raw beet sugar and the leaves of the Virginia creeper. It can be obtained by the distillation of catechin (cutch) and from certain resins or ortho-phenolsulphonic acid by fusion with potash, but is usually prepared from guaiacol by heating with hydriodic acid at  $200^\circ C$ . It is present to a notable extent in aqueous liquors from the low temperature carbonization of coal. It is crystalline, sublimable, and soluble in water, alcohol, and ether. It possesses antiseptic properties, and is used in photography. Vanillin can be obtained from catechol, and, by moist silver oxide, the unstable *ortho*-benzoquinone.

**CATECHU** (*Pale Catechu, Cutch, Gambier*) — An extract prepared from the leaves and young shoots of *Uncaria Gambier* (Fam. Rubiaceae), a climbing plant grown in the Malay Archipelago. It contains catechin and catechutannic acid and is used in medicine as an astringent. Black catechut or cutch is an extract prepared from the wood of *Acacia Catechu* (Fam. Leguminosae), a tree growing in Eastern India and Burma, used in dyeing, silk weighting and tanning.

**CATGUT** — Crude catgut is obtained from the intestines of sheep and other herbivorous animals. After removal, the intestines are split longitudinally into ribbons which are scraped to remove the mucosa

and muscular layers. According to the gauge of catgut required, one, two, or more ribbons are firmly and uniformly twisted to form a strand, which is then air-dried under tension and surface polished to produce a uniform diameter throughout its length.

Crude catgut is particularly liable to bacterial contamination with resistant spore-bearing organisms such as those responsible for gas-gangrene and tetanus. Great care must therefore be taken in the sterilization of catgut for surgical use. Heat processes are generally used for this purpose and since catgut consists mainly of collagen, it is essential that it should be thoroughly dried before the heat process is carried out. There would, otherwise, be a loss of tensile strength due to hydrolysis of the collagen. After drying, the crude catgut is placed in glass tubes which are filled with toluene, plugged, and heated for several hours at 160° C. to sterilize. The toluene is then replaced by water containing from 3 to 5 per cent. of ethyl alcohol and the tubes are sealed hermetically. Catgut packed in this manner is known as "non-boilable catgut" and is the form most commonly used since the aqueous fluid keeps it supple and flexible. "Boilable catgut" is packed in toluene and is so called because the outside of the container can be sterilized by immersion in boiling water.

Instead of sterilization by heat, chemical methods are sometimes used. One process consists of immersing the crude catgut in an aqueous solution containing 1 per cent. of iodine with potassium iodate and glycerin for 8 to 9 days until it has absorbed 12 per cent. of its weight of iodine. It is then immersed in a sterile bleach containing sodium thiosulphate to remove excess free iodine. The strands of sterilized catgut are then thoroughly washed, dried by dehydration with spirit and transferred aseptically to sterile glass tubes which are then hermetically sealed.

In order to delay its rate of absorption in the body, catgut may be treated with chromic acid or other suitable compound. The process is carried out on the dried crude catgut and various substances have been used for the purpose. Formerly, catgut so treated was marketed as 10, 20, or 30-day catgut according to the length of time required for it to be absorbed in the body. It is now generally agreed that tests for the length of time of absorption are unreliable and no specification of the absorbability is given other than the designation "chromic" or "hardened chromic." After undergoing the chromicizing process, the catgut is subjected to one of the sterilization processes described above.

Surgical catgut is subjected to stringent tests to ensure its suitability for use in operations on the human body. In accordance with the Therapeutic Substances Regulations, it can only be manufactured under licence and must comply with tests for sterility. It is, also tested for uniformity of diameter and tensile strength.

**CATHIONS (Cations)** — See Electricity (Electrochemical Aspects).

**CATHODE** — See Electricity (Electrochemical Aspects).

**CATHODE RAYS** — See Radioactivity.

**CAT'S EYE** — A quartz ( $\text{SiO}_2$ ) of translucent appearance found in Ceylon.

**CATTLE FOODS** — See Feeding Stuffs.

**CAUSTIC POTASH** — Potassium hydroxide. (See Potassium (Hydroxide).)

**CAUSTIC SODA** — Sodium hydroxide. (See Sodium (Hydroxide).)

**CAYENNE** — See Capsicum.

**CEDAR-LEAF OIL**, from *Juniperus virginiana*, contains limonene, cadinene, borneol, etc.; has a sp. gr. of 0.883 to 0.888 at 15° C., opt. rot. +55° to +65° at 20° C., and is soluble in alcohol and ether. The commercial oil is stated to be often derived from *Thuja occidentalis*. The oil of *Librocedrus bidwillii* of New Zealand, extracted from the leaves, has been shown to consist of terpenes 30 per cent. (*d*-pinene being the chief one) and 70 per cent. sesquiterpenes.

**CEDAR-WOOD OIL**. — A pale yellow essential oil of agreeable odour, used in perfumery and as an insectifuge, distilled from the wood of the *Juniperus virginiana*, *J. procera*, etc., to the extent of about 16 ozs. per cwt. Sp. gr., about 0.940 to 0.960 at 15° C.; opt. rot., -25° to -45°; ref. ind., 1.495 to 1.510 at 20° C. It is soluble in alcohol and ether, and contains as the chief constituent a crystalline substance named cedar-camphor together with the sesquiterpene cedrene ( $\text{C}_{15}\text{H}_{24}$ ).

**CEDRENE** — See Cedar-Wood Oil, and Hydrocarbons (Terpenes).

**"CELANESE"** — The trade-mark name of certain cellulose acetate silk goods. (See Silk Substitutes.)

**CELERY OIL** — Distilled from the fruit of *Apium graveolens*, having a sp. gr. of from 0.87 to 0.895. The yield is 0.2 per cent.; it has the odour and taste of celery, is soluble in alcohol, ether, etc., contains from 2 to 3 per cent. of a substance named lactone sedanolide ( $\text{C}_{12}\text{H}_{18}\text{O}_2$ ) (to which it owes its odour), associated with other substances, and is used for flavouring purposes.

**CELESTINE (Celestite)** — Native strontium sulphate ( $\text{SrSO}_4$ ), of crystal system No. 4, and sp. gr. 3.9; it takes its name from its colour, and fine specimens are found in Sicily. (See Strontium.)

**"CELITE"** — Preparations used as filter-aids, including "Super-cel."

**"CELLITE"** — The name of products prepared from a large deposit of hydrated amorphous silica on the Pacific coast in California, consisting of the skeletons of marine diatoms, useful for making insulating furnace linings and bricks. (See Kieselguhr.)

**CELLOPHANE** (Du Pont) — Cellulose acetate film and cellulose film. The latter film is made in various colours and of various light transmissions, which adapt it to retarding rancidity in food materials exposed to light when it is used as wrapper. (See Viscose.)

**“CELLOSOLVE” (UCC)** — Trade-mark for glycol-ether type of solvents for cellulose esters and ethers, natural and synthetic resins, and gums. (See Monoethyl, Monobutyl, and Monomethyl Ethers of Ethylene glycol.)

**CELLULOID (Xylonite)** — In the preparation of this material, cellulose (usually in the form of paper) is nitrated with a mixture of sulphuric and nitric acids until the nitrogen content amounts to about 10 to 11 per cent., and after bleaching, washing, and drying, it is gelatinized with a mixture of synthetic or natural camphor dissolved in alcohol, at which stage any colouring matters may be introduced as desired. It is then manipulated on hot rollers, and pressed into blocks or other forms. The optimum camphor content of celluloid is about 20 per cent., and various substances are introduced in addition to act as stabilizing and plasticizing agents. It is a plastic material at 75° C., and after evaporation of the solvent and upon cooling can be turned on a lathe. Celluloid is soluble in acetone, amyl acetate, hexalin acetate, isobutyl acetate, and other solvents. It is largely used for making combs, brush and knife handles, piano-keys, billiard balls, collars, mud-guards, toys, etc. The celluloid used in making cinematograph films is of a more highly nitrated character, while the proportion of camphor incorporated is smaller, but it is much more inflammable in character. Celluloid is easily inflammable, and only becomes plastic at a temperature not far below that at which it decomposes. On account of these objections, celluloid is becoming displaced by such plastics as “Bakelite,” and nylon. (See Cellulose, Dopes, Explosives (Gun-Cotton), Nitrocellulose, and Pyroxylin.)

**CELLULOSE** ( $C_6H_{10}O_5$ )<sub>n</sub> — The structural and preponderating tissue forming the walls or skeletons of plants, convertible into sugar, and extensively employed in the manufacture of paper, gun-cotton, nitro-cellulose, collodion, lacquers, and silk substitutes; also in compounding celluloid articles, and the preparation of celluloid and cellulose acetate films. (See Dopes, Explosives, and Pyroxylin.) Cellulose from purified cotton linters prepared by the viscose process has proved a good substitute for the usual sausage skins derived from animal intestines. Modifications of cellulose are largely used, amongst other applications, in the making of food containers and wrappers.

Cotton contains about 90 per cent. cellulose, and the proportion in woods of various sorts ranges from about 40 to 60 per cent. (See Paper.)

According to the micelle theory, cellulose is based upon glucose residues aggregated into chains of from 50 to 100 units, some 30 to 50 of these chains being further united, forming complex bundles or micelles. The investigations of Bragg and his associated workers using X-ray methods make it appear that cellulose is composed to a great extent of a mass of crystals and that in each crystal there is a periodicity parallel to the direction of the fibre, thus supporting the chemical evidence of a long chain of many links and suggesting the possible synthesis of sugars and the condensation of sugars into cellulose. The several varieties of cellulose are substantially identical in

cuprammonium solution with normal cotton cellulose, and from the optical and mass action relationships it reacts in its simplest chemical structural form,  $C_6H_{10}O_5$  (K. Hess).

When heated to  $260^\circ$  to  $270^\circ$  C. in a paraffin bath cellulose begins to decompose, but in common with wood and starch it can be distilled completely, according to H. E. Fierz-David, when admixed with sufficient nickel oxide and heated in hydrogen under a pressure of 100 to 250 atmospheres. (Compare Berginization.) Cellulose is stated to dissolve in sulphuric acid at concentrations between  $H_2SO_4.H_2O$  and  $H_2SO_4.3H_2O$  at ordinary temperatures without charring, and from a colloidal solution in 62 per cent.  $H_2SO_4$  it can be precipitated by dilution with water, alcohol, ether, or electrolytes. By the action of sodium hydroxide on cellulose, an additive compound (alkali cellulose,  $C_6H_9O_4.ONa$ ) is said to be formed. The absorption of sodium hydroxide from aqueous solution (2 to 8 per cent.) by cotton occurs rapidly, and the maximum effect is produced by concentrations of 20 per cent. and over, a process used in mercerizing cotton.

Cellulose on complete hydrolysis with dilute sulphuric acid yields the theoretical quantity of glucose, and all forms of cellulose, it is alleged, yield the same trimethyl cellulose when completely methylated.

Celluloses used for industrial purposes are of three classes—viz., the so-called pecto-celluloses, such as cotton, ramie, flax, and hemp; the ligno-celluloses, such as jute and the various woods; and, lastly, cereal straws and grasses. Ramie and hemp contain about from 63 to 66 per cent. cellulose. It is accompanied in vegetable matters with other nearly associated substances, namely, vasculose or ligno-cellulose, pectose or pecto-cellulose, and cutose, all of which are attacked by various chemical reagents to which cellulose is indifferent. Various methods are used for preparing cellulose according to the applications to be made of the product, including treatment of the vegetable matter with (1) caustic soda solution, (2) calcium bisulphite-sulphurous acid solution, (3) sodium sulphide-sodium hydroxide solution, and (4) chlorine. Gaseous, liquid, and aqueous solutions of chlorine are all used in various methods of preparing cellulose from its different sources.

To prepare pure cellulose, Cross and Bevan boil the raw material with a 1 to 2 per cent. solution of caustic soda, and, after washing, expose the undissolved portion to gaseous chlorine, and again boil the product with dilute alkali, thus eliminating all the non-cellulosic constituents (hemicelluloses, pectic compounds, lignin, and cutose), and yielding pure white cellulose.

Cellulose is soluble in an ammoniacal solution of cupric oxide (Schweitzer's solution), and this solution readily dissolves cotton and linen fibres; advantage being taken of this solubility in the manufacture of "Willesden paper," which is prepared by moistening the surface of a coarse paper with this solution after the surface has been gelatinized.

The etherification of cellulose can be effected, using alkali and alkyl bromides or iodides, by heating in a closed vessel for several hours, and

the products are of increasing interest for making photographic film-stock and lacquers.

The nitration of cellulose is referred to under the headings of Colloid, Cotton, Explosives, Nitrocellulose, and Pyroxylin. For the production of sugar and alcohol from cellulose see the articles Alcohol, Sugar, and Glucose, and the Report for 1925 of the Fuel Research Board (H.M. Stationery Office). *Other References*: "Cellulose," by C. F. Cross (Institute of Chemistry Lecture); "The Micelle Chemistry of Cellulose," by C. J. J. Fox (*J.S.C.I.*, **49**, 83 T (1930)); "Cellulose—The Rival of Coal Tar as a Raw Material," by A. J. Hall (*Ind. Chem.*, **7**, 355, 397, 508 (1931)); "Cellulose Resources," by G. M. Rommel (*Ind. Eng. Chem.*, **20**, 494, 587, 716 (1928)); "Structure of Cellulose," by H. D. Smith (*Ind. Eng. Chem.*, **29**, 1081 (1937)); *Researches on Cellulose*, by Cross and Dorée (Longmans, Green and Co., London); *Technology of Cellulose Esters*, by E. C. Worden (Spon and Co., London); *Chemistry of Cellulose and Wood*, by A. W. Schorger (McGraw-Hill Book Co., New York); *The Chemistry of Cellulose*, by Emil Heuser (McGraw-Hill Book Co., New York); *The Methods of Cellulose Chemistry*, by Charles Dorée (D. Van Nostrand Co., New York); *The Polysaccharides*, by R. J. McIlroy (Longmans, Green and Co., New York and London); *An Introduction to the Chemistry of Carbohydrates*, by Honeyman (Clarendon Press, Oxford); *Cellulose and Cellulose Derivatives*, by Emil Ott, editor (Interscience Publishers, New York).

See also Cellophane, Dopes, Films, Glucose, Lacquers, Lignin, Paper, Plasticizers, Silk Substitutes, Tall Oil, and Wood.

**CELLULOSE ACETATE (Sericose)** is a yellowish, non-inflammable substance prepared by the acetylation of cellulose in varying degrees. It is soluble in acetone and some other solvents in different amounts, and is used in making cinematograph films, dopes, and silk substitutes. The action of acetic anhydride in the presence of sulphuric acid upon cellulose leads to the production of a number of distinct bodies. The triacetate is the most important product. The processes are carried out by the action of acetic acid and its anhydride on dry cellulose in presence of a dehydrating agent such as sulphuric acid, zinc chloride, or phosphoric acid.

Applied as dope to wire netting, it is used as a substitute for glass under the name of "Spondite"; it is also largely used in making lacquers, construction of storage batteries, and in sheet form under the name of "Cellon." With respect to dyeing of cellulose acetate and silk substitutes, see Silk Substitutes. (See T. E. Ellison on "Viscosity of Cellulose Acetate Solutions" (*Chem. and Ind.*, **52**, 134 (1933)); H. Levinstein on "Cellulose" (*Chem. and Ind.*, **52**, 650 (1933)); *Cellulose Acetate: Its Manufacture and Applications*, by A. G. Lipscomb (Ernest Benn, Ltd., London); Cellophane, Lacquers, and Silk Substitutes.)

**CELLULOSE SPONGE (Du Pont)** — A sponge-like cellulose product that is highly absorbent, and soft when wet. It is made in various sizes of pore for washing and cleaning.

**"CELLUTYL" COLOURS** — Dyestuffs for cellulose acetate silk.

"**CEL-O-GLASS**" (Du Pont) — Trade-mark for plastic-coated wire cloth. Used for storm windows and doors, cold frames, and display backgrounds.

"**CEL-O-SEAL**" (Du Pont) — Cellulose film specially adapted for sealing closures on packaged foods, drugs, chemicals, and beverages.

"**CELOTEX**" — An artificial building board, made from Bagasse. (See Sugar.)

"**CELTA**" — A French variety of silk substitute.

**CELTUM** — See Hafnium.

**CEMENT (Portland Cement)** is prepared by the wet process from a mixture of alluvial clay (shales sometimes replacing the clay) and calcium carbonate or chalk (using about 76 to 78 per cent. of the latter), ground together in water. After allowing the mixture to settle, the water is poured off, the deposit is calcined in rotary kilns of great length, and then ground dry ready for use. It contains tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite in approximately the same proportions as would be calculated from the oxide composition. (See phase diagram and model, page 141, and R. H. Bogue (*Ind. Eng. Chem.*, **27**, 1312 (1935))). L. T. Brownmiller and R. H. Bogue present an X-ray study of Portland cement in *American Journal of Science*, **20**, 241 (1930). The clinker has a sp. gr. of 3.17, and on average contains about 22 per cent. silica ( $\text{SiO}_2$ ), 62 per cent. lime ( $\text{CaO}$ ), and 7.5 per cent. alumina ( $\text{Al}_2\text{O}_3$ ). The analysis of one particular brand of Portland cement is:  $\text{CaO}$  64.1 per cent.,  $\text{SiO}_2$  21.2 per cent.,  $\text{Al}_2\text{O}_3$  5.4 per cent.,  $\text{Fe}_2\text{O}_3$  4.8 per cent.,  $\text{MgO}$  2.2 per cent.,  $\text{SO}_3$  1.7 per cent.

When mixed with a small proportion of water, Portland cement forms a hard, tenacious mass which expands as it solidifies ("sets"), and—unlike ordinary mortar—can be used for hydraulic purposes. The setting is accelerated by rise in temperature. The rates of contraction and heat evolution in the setting of Portland cement are discussed by W. C. L. Hemeon in a paper in *Ind. Eng. Chem.*, **27**, 694 (1935). Storage of cement prolongs the time of initial and final setting, and rapid hardening depends largely upon the fineness of division of the constituent materials employed.

In the dry process, as described by C. G. Carter, limestone crushed to pass a 20-mesh sieve and thoroughly dried is mixed with dried clay in the required proportions and clinkered at 2,600° F. The mix contains some 42 per cent. lime, and at this temperature the lime combines with the silica, iron, and alumina. The product is preserved in this form until required and then mixed with 4 per cent. gypsum to lengthen the setting time of the cement, ground in comminutors and tube mills, thus furnishing the finished cement.

The partial use of blast-furnace slag in the manufacture of cement is largely practised in the North of England and Scotland, where suitable clays or marls are rare, and is said to give additional strength. Wennerstrom's method consists in heating the slag with lime in a graphite-lined circular furnace, while R. Grün first of all converts the

# CEMENT

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## CEMENT, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country				Cement Millions of Metric Tons	
Germany-Austria	..	..	..	14.7	
United Kingdom	..	..	..	7.6	
Italy	..	..	..	4.6	
France	..	..	..	4.3*	
Belgium	..	..	..	2.9	
Poland	..	..	..	1.5	
Sweden	..	..	..	1.0	
Czechoslovakia	..	..	..	1.0*	
Spain	..	..	..	0.8	
Denmark	..	..	..	0.7	
Yugoslavia	..	..	..	0.7	
Switzerland	..	..	..	0.6	
Netherlands	..	..	..	0.5	
Finland	..	..	..	0.5	
Rumania	..	..	..	0.5	
Hungary	..	..	..	0.4*	
Portugal	..	..	..	0.3	
Norway	..	..	..	0.3	
Greece	..	..	..	0.3	
				<hr/>	43.2
U.S.S.R.	..	..	..		5.6
U.S.A.	..	..	..	19.9	
Canada	..	..	..	0.9	
Mexico	..	..	..	0.4	
				<hr/>	21.2
Argentina	..	..	..	1.1	
Brazil	..	..	..	0.6	
Chile	..	..	..	0.4	
				<hr/>	2.1
Japan	..	..	..	6.0	
British India	..	..	..	1.0*	
Korea	..	..	..	0.9*	
Manchuria	..	..	..	0.8*	
China	..	..	..	0.5	
Turkey	..	..	..	0.3	
Indochina	..	..	..	0.3	
				<hr/>	9.8
Union of South Africa	..	..	..	0.9	
Egypt	..	..	..	0.4	
				<hr/>	1.3
Australia	..	..	..		0.8
Sum of above	..	..	..		84.0
WORLD PRODUCTION	..	..	..		88.7
Estimated.					

slag into a basic compound by adding alumina to the charge either before or with the lime, thus reducing the melting-point of the mixture and enabling it to take up more lime. The product, when finely ground with clinker, is stated to make a good cement.

According to Desch, the setting of wetted cements results from the decomposition of the aluminates into colloidal alumina and of the tricalcium silicate into the monocalcium silicate and calcium hydroxide, which slowly crystallizes in a colloidal matrix. In course of time the hydroxide is converted by the absorption of carbon dioxide from the air into carbonate, thus increasing the hardness of the product and its tensile and compression strength; also that of concrete made from it. The setting time of cement does not change of itself even after prolonged storage out of contact with air, while the time of "set" appears to depend upon the proportion of combined water present in hydrated calcium aluminate or silicate forming a protective sheath round the cement particles, thus resisting or delaying the penetration of water to the active core.

The lime which is set free during the setting of Portland cement, like the slaked lime of ordinary mortar, is capable of entering into combination with silica when presented to it in a sufficiently active form, and good cement can therefore be improved by the addition of a suitable pozzolanic substance. This circumstance also explains why the rapid hardening and maturing of newly made concrete is effected by the application of a dilute solution of sodium silicate. Pozzolanic materials are of volcanic origin, but others are used as substitutes (such as trass, granulated slag, baked slag, and spent shale), and are suitable so long as they contain silica and alumina in active form.

The only single substance so far found to constitute a perfect cement of itself is represented by the formula  $3\text{CaO} \cdot \text{SiO}_2$ , but the temperature required to make it is too high to be commercially available to advantage; admixture of alumina brings down the required temperature to some extent, but even with a mixture of the three oxides in the simple proportions,  $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ , the lowest temperature required is  $1,335^\circ \text{C}$ .

The "Ferrocrete" brand of cement is of rapidly hardening quality, the strength of which at twenty-four hours is stated to be beyond that required by the British standard specification at an age of seven days, whilst concrete made with it is alleged to be stronger at four days than one made with ordinary Portland cement at an age of twenty-eight days. It is of great breaking-load resistance and used in road-making and general construction work. The "Snowcrete" brand is a white variety, valued for use with reconstructed or artificial stone.

It is ordinarily understood that, to resist sea-water action, the alumina content should be kept low, but the French product known as "Ciment Fondu," which fuses at about  $1,400^\circ \text{C}$ ., and contains a large proportion of alumina, is stated to exhibit remarkable resistance to the decomposing influence of sea-water. Its composition (1), as given by H. F. Knight, and that of regular Portland cement (2) in France are given side by side:

	(1)	(2)
	Per cent.	Per cent.
Insoluble .. .. .	0.92	—
Silica .. .. .	9.76	23.0
Alumina .. .. .	44.32	7.0
Ferrous oxide .. .. .	0.47	—
Iron (calculated as metal) .. .. .	3.43	4.0
Lime .. .. .	40.26	64.0
Magnesia .. .. .	0.57	—
Sulphur (as sulphide) .. .. .	0.11	—
Alkalis, loss, etc. .. .. .	0.16	—
Other constituents .. .. .	—	2.0
	100.00	100.0

"Ciment Fondu" has a sp. gr. of 3.049 and a hydraulic modulus of 1.21, the figures approximating to the formula,  $2\text{Al}_2\text{SiO}_5, 6\text{Ca}_3\text{Al}_2\text{O}_6, 3\text{CaAl}_2\text{O}_4$ . It exhibits great tensile strength, rapid hardening, indifference to temperature as to setting, and makes concrete much superior to Portland cement concrete, capable of phenomenal loading quality, and immune to the attacks of sea-water and sulphur-impregnated water.

Calcium aluminate cements are manufactured by fusing bauxite and lime together in an electric furnace, and while the amount of lime in all Portland cements ranges from 1.7 to 2.2 times the sum of the silica, alumina, and ferric oxide, the ratio in the aluminate varieties is about 0.66. Again, the silica to alumina ratio in Portland cements is always over 2.5, while in the aluminate qualities the relationship is about 0.25. The "Lightning" brand of cement made by melting bauxite with lime is of highly aluminous character, a typical analysis showing 40 per cent. alumina, 40 per cent. lime, 10 per cent. silica, and 10 per cent. iron oxide. It is said to have great strength at 24 hours, being then as strong as ordinary Portland cement at a month or more, so that it is of special value when speed of construction is of paramount importance and for endurance in sea-water.

The so-called "Titan" cements are quick-hardening and of high strength, having a lime base like Portland and alumina cements, but with titania ( $\text{TiO}_2$ ) as their chief acid constituent in place of silica or alumina. They are made by fusing a mixture of titaniferous iron ore, limestone, and coke in an electric or a blast furnace, pig-iron being a by-product, while the slag, when finally ground, constitutes the cement. Probably they can be economically made where titaniferous magnetite is abundant, as in the Saguenay district in Quebec.

Keene's cement is stated to be produced by the calcination of gypsum or the recalcination of the partially calcined material which has been made to take up a quantity of aluminium sulphate or alum solution.

Roman cement is made from natural mixtures of lime and clay, such as septenium (cement stone), by calcination in kilns with subsequent grinding and sifting. It has quick-setting property which makes it

valuable for work requiring rapid erection—as, for instance, on work between tides—but is only of medium strength. (See Septaria.)

*References:* "The Setting of Portland Cement," by P. S. Roller (*Ind. Eng. Chem.*, **24**, 1077 (1934)); "Cement Progress and Research," by R. W. Carlson (*Ind. Eng. Chem.*, **27**, 638 (1935)); E. C. Eckel on *Cements, Limes, and Plasters* (Chapman and Hall, London); R. K. Meade on *Portland Cement* (Chemical Publishing Co., Brooklyn, Williams and Norgate, London); Robert H. Bogue on *The Chemistry of Portland Cement* (Reinhold Publishing Corp., New York); J. C. Witt on *Portland Cement Technology* (Chemical Publishing Co., Brooklyn). See also Adhesives, Bricks, Calcium (Plaster of Paris), Concrete, Lutes, Marine Glue, "Permac," "Prodorite," Red Lead, "Rostkitt," Sealing Wax, "Sorel Cement," Spence Metal, and White Lead.

**CEMENTITE** ( $\text{Fe}_3\text{C}$ ) — Iron carbide, a black hard solid, of m.p.  $1,837^\circ\text{C}$ ., formed by reaction of iron and carbon at high temperature, and an important constituent of steel.

**CENOSHERES** (of Coke) — See Coal, and Coke.

**CENTI** — Prefix signifying "a hundredth of" in the metric system.

**CENTIGRADE** — See Heat.

**CENTIMETRE** — See Weights and Measures.

**CENTIPOISE** — One-hundredth of a poise, the unit of viscosity. Water at  $20^\circ\text{C}$ . has a viscosity of 1.0087 centipoises. One poise equals one dyne-second per square centimetre, the c.g.s. unit of absolute viscosity.

**CENTISTOKE** — One-hundredth of a stoke, which latter is the c.g.s. unit of kinematic viscosity (absolute viscosity *divided by* density).

**CENTRIFUGE** — A machine for separating the constituents of liquid suspensions or emulsions by centrifugal force. It is in effect either an accelerated filter or an accelerated settler. Machines of the first type have a perforated revolving basket lined with filter medium, into which the liquid is introduced. They are used to separate relatively coarse solids. For fine suspensions and emulsions the second type is preferred, having an impermeable bowl. Various arrangements of cones and baffles within the bowl increase the length of travel of the liquid and reduce the settling distance.

Centrifugal force is commonly described as being  $N$  times that of gravity.  $N = V^2/gR$ , where  $V$  = linear velocity of rotation in ft./sec.,  $R$  = radius of rotation in ft.,  $g$  = acceleration of gravity ( $32.2\text{ ft./sec.}^2$ ). While centrifugal force is proportional to  $V^2/R$ , the tensile stresses generated in the material of the bowl vary with  $V$  only; hence for high values of  $N$  it is mechanically advantageous to have a bowl of small diameter running at high speed. Such "super-centrifuges" can generate centrifugal forces up to  $N=17,000$ . They are used for clarifying varnish, dewaxing lubricating oil, and the separation of various suspensions and emulsions.

See *Centrifugal Dryers and Separators*, by E. A. Alliot (Ernest Benn, Ltd., London); *The Ultracentrifuge*, by The Svedberg and Kai O. Pederson (Oxford Univ. Press); *Particles, Porcelain, and Separation*.

**CEPHALINE** ( $C_{28}H_{38}O_4N_2$ ) — An alkaloid of m.p.  $120^{\circ}$ – $130^{\circ}$  C. (anhydrous). (See *Ipecacuanha*.)

**CERAMICS** — Pertaining to pottery. (See publications of the Ceramic Society; "Ceramic Linings for Chemical Equipment," by P. C. Kingsbury (*Trans. Inst. Chem. Eng.*, **12**, 248 (1934)); *Ind. Eng. Chem.*, **29**, 402 (1937); *Encyclopædia of the Ceramic Industries*, by A. E. Searle (E. Benn, Ltd., London); *Ceramic Chemistry*, by H. H. Stephenson (Davis Bros., Manchester); *Clay and Pottery Industries*, by J. W. Mellor (C. Griffin and Co., London); *Ceramics—Clay Technology*, by Hewitt Wilson (McGraw-Hill Book Co., New York); *The Clay-worker's Handbook*, by A. E. Searle (C. Griffin and Co., London); also Bricks, Clays, Glass, Porcelain, Refractories, Silica, and Stoneware.)

**CERARGYRITE** — See Horn Silver.

**CEREAL CHEMISTRY** — See Amylases, Foods, and Wheat.

**CEREBRINE** — See Brain Matter.

"**CERESAN**" (Du Pont) — Trade-mark for seed disinfectant based on ethyl mercury para-toluene sulphonanilide. Used as a dust or slurry for the treatment of wheat, oat, barley, rye, pea, sorghum, cotton, sugar beet, and flax seeds.

**CERESINE** — See Ozokerite, and Waxes.

**CERITE** — A rare mineral, of crystal system No. 4, and sp. gr. 4.75 to 5, found in Sweden, being a hydrated silicate of cerium, containing also lanthanum and praseodymium, from which cerium is extracted.

**CERIUM (Ce) and its Compounds** — Atomic weight, 140.13. See Elements for other data. Cerium is found in association with lanthanum in the Swedish minerals *cerite*, *allanite*, and *orthite*, also in *gadolinite*, *wöhlerite*, and *monazite*. It is malleable, ductile, resembles iron in appearance, oxidizes quickly in moist air, forms alloys with iron, aluminium, zinc, magnesium, and combines with boron and silicon. It is made by electrolysis of the fused chloride.

There are three **oxides**:  $Ce_2O_3$ ;  $CeO_2$  (ceria), used in the preparation of mantles for use in incandescent gas lighting and as an abrasive; and  $CeO_3$ . Cerium exhibits prevailing valencies of +3 (cerous) and +4 (ceric).

**Cerous Nitrate** ( $Ce(NO_3)_3 \cdot 6H_2O$ ) is a pink crystalline salt soluble in water; the **chloride** ( $CeCl_3$ ) is a colourless crystalline compound also soluble in water; while **cerous ammonium nitrate** ( $Ce(NO_3)_3 \cdot 2NH_4NO_3 \cdot 4H_2O$ ) is a white crystalline soluble salt; all three compounds are used in the preparation of incandescent gas mantles.

**Ceric Nitrate** is itself unstable, but the double salt  $(NH_4)_2Ce(NO_3)_6$  is obtainable in well-defined orange crystals.

**Ceric Sulphate** ( $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) is a reddish-yellow crystalline salt, and a powerful oxidizing agent; is soluble in water and used in volumetric analysis, and photography.

**Ceric Ammonium Sulphate** ( $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ) is used in volumetric analysis as an oxidizing reagent.

The **oxalate** ( $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$ ) and the insoluble **fluoride** ( $\text{CeF}_3 \cdot \text{H}_2\text{O}$ ) (by-products in the manufacture of thorium from monazite sand) are used in connection with searchlights and tracer bullets; the fluoride is also used in ceramics. The oxalate is but slightly soluble in water, and, in addition to its other uses, is employed medicinally for the prevention of chronic vomiting. Cerium compounds are also used as catalysts in making aniline black and as reducing agents in photography. (See Gas Mantles, also Iron (Ferrocerium).)

The **cerium group** of the rare-earth elements consists of scandium, lanthanum, cerium, praseodymium, neodymium, samarium, europium, and gadolinium, the potassium sulphate compounds of which are all insoluble or only slightly soluble in water. See Yttrium for the other group of rare-earth elements, and the individual elements.

*Reference: The Rare Earth Elements and Their Compounds*, by D. M. Jost *et al.* (John Wiley and Sons, New York).

**CEROTIC ACID** ( $\text{C}_{25}\text{H}_{51}\text{COOH}$ ) — A crystalline fatty acid, m.p.  $85^\circ\text{C}$ ., of the normal series, occurring, free and combined, in beeswax and many other waxes. It may be obtained from Chinese wax by fusion with potassium hydroxide or by dry distillation, and from paraffin wax by oxidation with chromic acid. (See Waxes (Beeswax).)

**CEROTIN** — Chinese Wax. (See Waxes.)

**CERULEAN BLUE** — A light blue pigment or artist's colour made by heating together copper sulphate, tin oxide, and precipitated silica or chalk.

**CERUSE** — Lead carbonate or white lead.

**CERUSSITE** — A mineral lead carbonate ( $\text{PbCO}_3$ ) occurring in Cornwall, Cumberland, Siberia, and the U.S.A., of crystal system No. 4, and sp. gr. 6.5. (See Lead.)

**CERYL CEROTATE** ( $\text{C}_{25}\text{H}_{51}\text{COOC}_{26}\text{H}_{53}$ ) — A constituent of Chinese wax, which has also been isolated from sunflower oil. (See Cerotic Acid.)

**CESIUM (CÆSIUM) (Cs) and its Compounds** — Atomic weight, 132.91. See Elements for other data. Cesium belongs to the group of alkali metals, and is found in association with potassium and sodium in some alkali minerals (including *porphyrites*, *lepidolites*, and *carnallite*), also in certain mineral waters, but the best source is the mineral *pollux*, or *pollucite*, in which it is contained in the form of a compound silicate of aluminium and cesium, yielding from 31 to 37 per cent. of the oxide.

Cesium is a silver-white, soft, ductile metal, which readily tarnishes by oxidation in the air and therefore has to be kept in naphtha. It is used in making thermionic valves.

Compounds of cesium resemble those of potassium ; they include the **carbonate** ( $\text{Cs}_2\text{CO}_3$ ), which is white, soluble, and used in the mineral-water trade ; the **chloride** ( $\text{CsCl}$ ), a colourless, soluble, crystalline salt similarly used, and in medicine ; the **nitrate** ( $\text{CsNO}_3$ ), a white crystalline salt soluble in water ; the four **oxides**,  $\text{Cs}_2\text{O}$ ,  $\text{Cs}_2\text{O}_2$ ,  $\text{Cs}_2\text{O}_3$ , and  $\text{Cs}_2\text{O}_4$ , all of which are yellow or red, except  $\text{Cs}_2\text{O}_3$ , which is chocolate brown ; the **silicate** ( $\text{Cs}_2\text{SiO}_3$ ), insoluble, and used in ceramics ; and the **sulphate** ( $\text{Cs}_2\text{SO}_4$ ), a colourless crystalline salt soluble in water, used in brewing and making mineral waters.

Cesium compounds that can be volatilized, especially the chloride, impart a violet colour to the Bunsen flame.

**CETANE RATING** — The detonation characteristic of liquid fuels for diesel engines is based on a test of the fuel in a standard engine, specified by the American Society for Testing Materials (A.S.T.M.). In this test pure cetane (normal hexadecane,  $n\text{-C}_{16}\text{H}_{34}$ ) gives a "cetane number" of 100 and *alpha*-methyl-naphthalene ( $\text{C}_{10}\text{H}_7\cdot\text{CH}_3(I)$ ) 0, and mixtures of these two hydrocarbons give intermediate numbers proportionally. For spark-fired engines a corresponding test is the octane rating (see same). (See Diesel Oil.)

"**CETAVLON**" — See Cetrimide.

**CETIN** — See Waxes (Spermaceti).

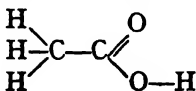
**CETOSTEARYL ALCOHOL** — A mixture of the higher, aliphatic alcohols, chiefly cetyl and stearyl alcohols, prepared by the reduction of sperm oils or the fatty acids obtained from coconut oil. It is used in pharmacy as an emulsifying agent in combination with sodium laurylsulphate.

**CETRIMIDE** ("C.T.A.B.", "Cetavlon") — A slightly off-white powder, principally cetyltrimethylammonium bromide ; soluble in water. Used as a bactericide and detergent.

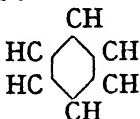
**CEVADINE** — See Veratrine.

**CHAIN REACTION** — A term applied to any chemical or nuclear reaction in which some of the products assist in the furtherance of the reaction. In the uranium power pile or the atomic bomb, the capture of a neutron by a uranium atom causes fission, which causes the release of more neutrons and further fission, and so on. At least one of the neutrons released by *each* fission must be utilized in producing another fission to produce a practical chain reaction.

**CHAINS** — Theoretical views of atomic arrangements of several classes. Open chains are regarded as having terminal atoms not mutually in combination, by which, for example, aliphatic combinations, such as the olefins and paraffins, are characterized ; thus, acetic acid is represented constitutionally by the formula :



In closed chains, the terminal atoms are regarded as mutually combined, forming a ring, as in benzene :



A "normal" (*n*-) chain is a through chain, without branches, whereas a chain with one or more branches is a "forked" chain. A chain with a single branch is called "*iso*." "Side" chains present a chain of atoms in combination with a longer chain either open or ring shaped. (See Acyclic, Aliphatic, Benzene Ring, Rings, and Valencies.)

**CHALCANTHITE** — Native copper sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), of crystal system No. 6, and sp. gr. 2.21, found in some Chilian mines, Arizona, etc.

**CHALCEDONY (Onyx)** — A variety of quartz, of crystal system No. 3, and sp. gr. 2.6, found in Bithynia and elsewhere. (See Silicon, and Cornelians.)

**CHALCOCITE (Redruthite)** — Mineral copper sulphide ( $\text{Cu}_2\text{S}$ ), of crystal system No. 4, and sp. gr. about 5.5. (See Copper.)

**CHALCOLITE** — A rare mineral ( $\text{CuO}, \text{UO}_3, \text{P}_2\text{O}_5, 8\text{H}_2\text{O}$ ), of crystal system No. 2, and sp. gr. about 3.5.

**CHALK** — See Calcium (Carbonate).

**CHALYBEATE WATERS** — Natural waters containing iron as ferrous carbonate in a state of solution, constituting valuable tonics in cases of debility. Such waters are found and used medicinally at Tunbridge Wells, Cheltenham, Harrogate, Leamington, Scarborough, Strathpeffer, and elsewhere.

**CHAMOMILE** — The dried flowerheads of *Anthemis nobilis* (Fam. Compositæ), a plant indigenous to Britain and cultivated in Hampshire, Surrey, France, and Belgium. It contains about 0.2 per cent. of a volatile oil, to which the odour is due ; formerly used in medicine.

**CHANCE PROCESS** — See Sulphur (Recovery).

**CHARCOAL** — See Carbon.

**CHARLES' LAW** — See Gas Laws.

**CHAULMOOGRA OIL** — A thick yellowish-brown oil or soft fat, of acrid taste, expressed from the seeds of *Hydnocarpus Kurzii*, m.p.  $33^\circ$  to  $39^\circ$  C., sp. gr. about 0.95, sap. v. 196 to 213, acid v. 21 to 27, and i.v. 98 to 104 ; soluble in alcohol, ether, and carbon disulphide. The seeds, which are imported from Burma, Assam, and Siam, yield about 33 to 50 per cent. of the oil, which consists mainly of the glycerides of chaulmoogric acid ( $\text{C}_{18}\text{H}_{32}\text{O}_2$ ), and hydnocarpic acid ( $\text{C}_{16}\text{H}_{28}\text{O}_2$ ), with smaller quantities of the glycerides of palmitic acid, taraktogenic acid ( $\text{C}_{36}\text{H}_{60}\text{O}_6$ ), and isogadoleic acid ( $\text{C}_{20}\text{H}_{38}\text{O}_2$ ). For further information concerning the glycerides of chaulmoogra oil see A. Bomer and H. Engel, *Analyst*, 54, 423 (1929). The ethyl esters of the fatty acids of

chaulmoogra oil are used in medicine for the treatment of leprosy. Gorli oil, obtained from *Oncoba echinata*, a native of Sierra Leone, French Guinea and the Ivory Coast of W. Africa, has been stated to afford a satisfactory substitute for chaulmoogra oil. It contains 75 to 80 per cent. of chaulmoogric acid, sp. gr. about 0.93 at 30° C., m.p. 40° to 42° C. (see Andre and Jonatte, *Analyst*, **53**, 604 (1928) ; for a description of Burmese species, see Peacock and Aiyar, *Brit. Chem. Abst.*, B, **1931**, 552 ; Bokil and Nargund on "The Synthesis of Chaulmoogric and Hydnocarpic Acids" in *Proc. Ind. Acad. Sci.*, **11A**, 409 (1940) ; Hydnocarpus Oil, "Moogrol," and Taifushi Oil.)

**CHEDDITE** — See Explosives.

**CHEESE** — of which there are many varieties—is ordinarily made from milk by coagulation with rennet, and represents its casein constituent with some of its butter. It undergoes chemical changes upon keeping, and is a valuable food. It varies in composition according to the milk from which it is made and to details in the process of manufacture, containing from 30 to 60 per cent. water,  $2\frac{1}{2}$  to  $5\frac{1}{2}$  per cent. nitrogen, from 19 to upwards of 45 per cent. fat, and from  $4\frac{1}{2}$  to 7 per cent. mineral substances (ash). Roquefort cheese is made from a mixture of sheep's and goat's milk, and Gruyère cheese, containing about from 40 to 45 per cent. fat (originally made from goat's milk), made from cow's milk. (See Casein, and Milk.)

**CHELATION (Cheliform)** — See Co-ordination, and Hydrogen Bonding.

**CHELIDONINE** — A colourless crystalline alkaloid ( $C_{20}H_{19}O_5N, H_2O$ ), extracted from *Chelidonium majus*, soluble in alcohol and ether, and which forms an additive hydrochloride soluble in water and alcohol ; both preparations are used medicinally. (See Sparteine Sulphate.)

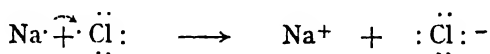
**CHEMICAL BONDS** — The combination of atoms to give a variety of molecules is of paramount importance in all chemical work. The bonds that bind one atom to another in a molecule are of paramount interest because an understanding of this phenomenon allows chemists to produce many compounds with desired properties. The rules of valence, as this is called, are fairly satisfactory for predicting the permissible ways that atoms can form compounds. Sometimes these rules are inadequate and empirical with the result that new concepts are introduced from time to time. Thus in 1916 G. N. Lewis proposed the "electron pair" theory, then Lewis, Kossel, and Langmuir proposed the "electron octet" hypothesis, and last but not least we have the attempts of quantum and wave mechanics to explain the chemical bonds that exist between atoms.

Originally valence was merely a number indicating the holding power of one type of atom for a standard atom, usually hydrogen ; for example, one oxygen atom holds two hydrogen atoms in water ( $H_2O$ ) so oxygen is said to have a valence of two. In like manner the valence of carbon is four in carbon dioxide ( $CO_2$ ), nitrogen is three in ammonia ( $NH_3$ ), and chlorine is one in hydrogen chloride ( $HCl$ ).

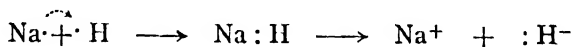
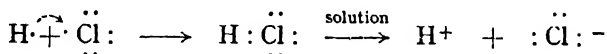
With the development of the electronic concept of atomic structure (see Atoms) the ideas of valence were tied in with the electrons existing in the outermost or valence orbits. Now the holding power of an atom is associated with the number of electrons that an atom will either give up or take on or share in a chemical combination.

Any attempt to explain chemical bonds must be based upon the experimental fact that some compounds are *non-polar* like methane and some are highly *polar* like the electrolyte, sodium chloride. In other words, the forces that hold *ions* together in electrolytes are quite different from those forces holding *atoms* together in organic molecules and in ions such as sulphate or nitrate.

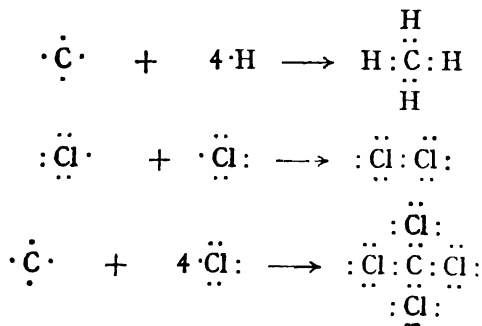
In highly polar compounds, like electrolytes, the forces are chiefly electrostatic giving rise to *ionic linkages* or heteropolar bonds. These bonds arise by the loss or gain of an electron from the valence shell, thus :



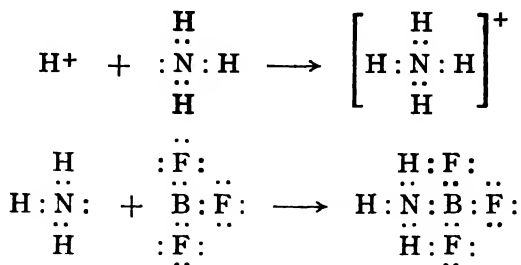
which is to be read : an *atom* of sodium, having one valence electron (indicated by a dot), reacts with an atom of chlorine, having seven valence electrons (indicated by seven dots), by giving its one valence electron to chlorine and becoming a *positive* sodium *ion* (indicated by +) while the chlorine becomes a *negative* chloride *ion* (indicated by -). These two charged ions make up the basic unit of the compound sodium chloride. In like manner :



The non-polar compounds involve a *homopolar bond* or *sharing of an electron pair* which gives rise to an "exchange energy" understandable upon the basis of quantum mechanics. For example, a *covalent bond* can exist when each atom furnishes one electron to an electron pair which is mutually shared by the two atoms as follows :



Some atoms form non-polar linkages, called *co-ordinated covalency*, by sharing electron pairs that are contributed entirely by one atom. For example :



It should be pointed out that in nearly all linkages between atoms both electrostatic and "exchange energy" bonds are operating simultaneously. In compounds there will be gradations between the two extremes. In order to explain the relationship between these two types of bond forces as they exist in compounds the concept of *resonance* is useful and can be quantitatively measured. By rapidly oscillating between various electronic configurations (*i.e.*, resonance), the electrons can give to the compound the properties that are observed. This concept has been very fruitful in the field of organic chemistry, for example, benzene ( $\text{C}_6\text{H}_6$ ).

Another concept of the electronic theory of valence is that of the *hydrogen bond*. The hydrogen atom is unique owing to the fact that when it loses an electron only the nucleus of very small diameter remains. The hydrogen nucleus is so small it apparently can attract two strongly negative atoms and thus establish a hydrogen bond between the two atoms, for example,  $\text{HF}_2^-$ .

By the electronic theory double and triple bonds of organic chemistry are denoted by sharing two and three pairs of electrons respectively, as in ethylene and acetylene.



A further study of the electronic theory of matter leads to the conclusion that electrostatic forces can arise from: (a) ion formation by electron addition or removal, (b) an unsymmetrical distribution of the electrical forces in the molecule, so that a *dipole* results, (c) an *induced dipole* due to the influence of an ion or dipole in the vicinity of an electrically symmetrical molecule. These three types of electrostatic binding give rise to six types of combinations in bonding atoms together as follows: (1) *Ion-ion* binding as in electrolytes. Ionic bindings are stronger than most homopolar forces and the compounds generally show rigidity. The ionic diameters play an important part in this bond, thus, hydrogen is held more firmly by fluoride (of small diameter) than by iodide (of large diameter) ions. (2) *Dipole-dipole* bindings.

Considerable energy is required to separate two unit dipoles when they are aligned in the normal way. This attraction leads to association of liquids such as water, and ethanol. (3) *Induced dipole-induced dipole* bindings. These small forces are generally unnoticed, but they are sufficient to allow helium to be liquefied at low temperatures. (4) *Ion-dipole* forces. The dissolving of electrolytes in water is due to these forces. (5) *Ion-induced dipole* forces. The formation of  $I_3^-$  ions and other complex ions is due to these forces. (6) *Dipole-induced dipole* forces. The solubility of certain inert gases in liquids is due to these forces of attraction.

*References:* *The Nature of the Chemical Bond*, by L. Pauling (Cornell University Press, Ithaca, New York); *Electronic Structure and Chemical Bonding*, by Rice (McGraw-Hill Book Co., New York); *Physical Chemistry*, by Moelwyn-Hughes (Cambridge University Press, Cambridge); *The Structure of Molecules and the Chemical Bond*, by Y. K. Sirkin and M. E. Dyatkina (Interscience Publishers, New York).

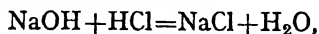
**CHEMICAL COMPOUNDS** — Several classes of compounds are described here. (See also Chemical Bonds.)

**Oxides, Hydroxides, Bases, and Salts** — The oxides include combinations of metals such as potassium, sodium, calcium, magnesium, and strontium with oxygen, and these oxides by combination with water form *hydroxides*, the potassium and calcium compounds being represented respectively as follows:

Oxides	Hydroxides
$K_2O + H_2O$	$2KOH$
$CaO + H_2O$	$Ca(OH)_2$

Ammonium hydroxide is a combination of 1 atom of nitrogen with 5 atoms of hydrogen and 1 atom of oxygen ( $NH_4OH$ ). These compounds, as also the carbonates (see Carbonic Acid), all behave as bases, and by interaction with acids form corresponding salts. (See Bases, and Oxides.)

When an acid solution is mixed with its equivalent quantity of an alkaline or other basic solution, the acid character of the one solution and the alkaline or basic character of the other solution are severally destroyed or *neutralized*. For example, if a solution of sodium hydroxide in water be mixed with one of hydrochloric acid, a chemical interaction takes place, and sodium chloride is produced in solution. This change is represented as follows:



and if the neutral solution which results from this reaction be heated so as to cause evaporation of sufficient water, the salt will be obtained in a crystalline condition upon cooling of the solution.

Similarly, when lime is treated with hydrochloric, nitric, or sulphuric acid, it enters into combination and forms the corresponding salts, namely, calcium chloride, nitrate, or sulphate, as the case may be. Thus, if hydrochloric acid be employed, the change is expressed as follows:  $CaO + 2HCl = CaCl_2 + H_2O$ ; with nitric acid as follows:

$\text{CaO} + 2\text{HNO}_3 = \text{Ca}(\text{NO}_3)_2 + \text{H}_2\text{O}$  ; and with sulphuric acid as follows :  
 $\text{CaO} + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + \text{H}_2\text{O}$ .

The chloride and nitrate of calcium are both soluble in water, but the sulphate is almost insoluble.

**Chlorides, Bromides, Iodides, and other Compounds**—If in place of oxygen, the elements chlorine, bromine, iodine, fluorine, and sulphur be severally taken and made to combine with metals or bases, the resulting compounds are *chlorides, bromides, iodides, fluorides, and sulphides*.

This is shown in tabulated form as below :

Compounds of	Called	Example	Formula
Oxygen	Oxides	Zinc oxide	ZnO
Chlorine	Chlorides	Sodium chloride	NaCl
Bromine	Bromides	Potassium bromide	KBr
Iodine	Iodides	Potassium iodide	KI
Fluorine	Fluorides	Calcium fluoride	$\text{CaF}_2$
Sulphur	Sulphides	Lead sulphide	PbS

The names used to identify chemical substances are designed to indicate their composition, but many old common or familiar names are still retained.

It frequently happens that the same two chemical elements combine together in various proportions, so forming as many different compounds, and to distinguish these, terminal letters or prefixes are employed. For instance, the two compounds water and hydrogen dioxide ( $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  respectively) are both composed of hydrogen and oxygen, so the one with the higher proportion of oxygen is styled hydrogen dioxide or peroxide, water being hydrogen monoxide.

Again, phosphorus combines with chlorine to form two chlorides  $\text{PCl}_3$  and  $\text{PCl}_5$ , and these are termed respectively *phosphorous* chloride and *phosphoric* chloride, or preferably phosphorus *trichloride* and phosphorus *pentachloride* respectively.

Acids are commonly called by their familiar names, but may be, and often are, described as compounds of hydrogen—for instance :

Hydrochloric acid = Hydrogen chloride.

Nitric acid = Hydrogen nitrate.

Sulphuric acid = Hydrogen sulphate.

The suffixes *ic* and *ous* are used to denote acids with the greater and smaller proportion of oxygen, where that element enters into their combinations ; thus we have : Sulphuric acid, formed from sulphur trioxide and water :  $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$  ; sulphurous acid, formed from sulphur dioxide and water :  $\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_3$  ; nitric acid, formed from nitrogen pentoxide and water :  $\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HNO}_3$  ; nitrous acid, formed from nitrogen trioxide and water :  $\text{N}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{HNO}_2$ .

When these acids combine with bases—for example, potassium oxide—they form respectively *sulphate, sulphite, nitrate, and nitrite* of

potassium ; or, instead of expressing them as named, they may be described as potassium sulphate, sulphite, nitrate, and nitrite, respectively.

Some metals, including copper, iron, mercury, and tin, form two compounds of most of the classes, and these are indicated by the terminations of the metallic names ; thus, ferric chloride is  $\text{FeCl}_3$ , and ferrous chloride is  $\text{FeCl}_2$  ; mercuric chloride is  $\text{HgCl}_2$ , and mercurous chloride is  $\text{Hg}_2\text{Cl}_2$ , and so forth. The names of the compounds containing the larger proportion of metal end with the termination *ous*, and those with the smaller proportion with the ending *ic*.

**Carbonates, Carbides, Nitrides, Hydrides, and Phosphides** are described under their respective headings.

**Silicon, Boron, and Selenium** in combination with metals form silicides, borides, and selenides, and the more important ones find description under other headings.

**Anhydrides** as a class are related to the acid-forming oxides, such as sulphur trioxide ( $\text{SO}_3$ ), which by combination with water gives sulphuric acid,  $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ . By abstracting or taking away the water from sulphuric acid it is reduced to its anhydride. The term, however, is used more generally. (See Anhydrides.)

**Cyanides** — See Cyanogen.

**Arsines, Phosphines, and Stibines** — Very oxidizable compounds formed by replacing hydrogen of hydrogen arsenide ( $\text{AsH}_3$ ), hydrogen phosphide ( $\text{PH}_3$ ), and hydrogen antimonide ( $\text{SbH}_3$ ) by hydrocarbon groups.

**Hydrosulphides** — See Hydrosulphides, and Nomenclature.

**Organic Compounds** — See Carbon.

**CHEMICAL CONSTANTS** — See Constants (Physico-Chemical), and Critical Points.

**CHEMICAL ELEMENTS** — See *Frontispiece*, and Elements.

**CHEMICAL ENGINEERING** — The science and art of designing, building, and operating plant for the manufacture of materials in bulk. Its field of usefulness is thus wider than the chemical industry, and includes such other process industries as smelting and metal refining, petroleum refining, cement manufacture, and brewing. The basis of chemical engineering is a scientific study of "unit operations," of which the principal are : Absorption, Adsorption, Calcination, Centrifugal Separation, Classification (by particle size), Combustion, Crushing and Grinding, Crystallization, Diffusion, Distillation, Drying, Electrolysis, Evaporation, Filtration, Fluid Flow, Heat Transfer, Leaching (Lixivation), Mixing, Refrigeration, Sedimentation, Solvent Extraction, Sublimation, Surface Catalysis. An engineer who understands these operations and the types of plant in which they are conducted can usefully apply his knowledge to any of the process industries.

In the theoretical analysis of unit operations and the design calculations that are based thereon, the engineer's chief tools are Material Balances, Heat or Energy Balances, and Velocity Equations. Material and heat balances help to provide information about the formal design of a plant ; for instance, the number of trays required in a fractionating

column in order to effect a given separation. Velocity equations define the rate at which the physical and chemical reactions which govern an operation proceed, and thus enable the engineer to calculate the size of plant required for a given throughput. Such equations have been worked out for most of the unit operations, often with the aid of dimensional analysis.

The practical duties of a chemical engineer include supervising the construction and operation of process plant, conducting semi-technical and large-scale experiments, locating and correcting plant troubles. Owing to the scale on which his operations are conducted, the chemical engineer must be continually mindful of costs; material, heat, power, labour, maintenance and overhead costs all come within his purview. He is often entrusted with executive responsibility, and should therefore know something of industrial management.

Chemical engineering began to emerge as a distinct profession in England towards the end of the 19th century. In 1879 a meeting of interested persons, including Professors Roscoe and Thorpe, defined a chemical engineer as one who "possesses chemical and mechanical knowledge and who applies that knowledge to the utilization on a manufacturing scale of chemical action." When the Society of Chemical Industry was formed in 1881, many members wished to call it the Society of Chemical Engineers. The first textbook was an excellent two-volume *Handbook of Chemical Engineering*, by George E. Davis, published by Davis Bros. of Manchester in 1901. Later, America took the lead in developing this branch of engineering, and in 1908 the American Institute of Chemical Engineers was formed. World War I brought about a revival of interest in England and led to the formation of the Institution of Chemical Engineers in 1922. America still kept her lead however, and to-day the standard general textbooks are American. A survey showed that about 10 per cent. of all American engineers are chemical engineers, and that they are the most highly paid group in the profession. Curiously, chemical engineering appears never to have established itself as a separate profession in Germany. The great chemical industry of Germany evolved by close co-operation between chemists and mechanical engineers. A similar situation exists in some British chemical companies.

*References*: Walker, Lewis, McAdams, and Gilliland, *Principles of Chemical Engineering* (McGraw-Hill Book Co., New York); J. C. Olsen, *Chemical Engineering* (D. Van Nostrand Co., New York); Badger and McCabe, *Elements of Chemical Engineering* (McGraw-Hill Book Co., New York); Hougan and Watson, *Chemical Process Principles*, 3 vol. (John Wiley and Sons, New York); G. G. Brown, *et al.*, *Unit Operations* (John Wiley and Sons, New York); Perry, *Chemical Engineers' Handbook* (McGraw-Hill Book Co., New York). These are referred to when "Standard Chemical Engineering Works" are mentioned.

*Periodicals*: *Transactions of the American Institute of Chemical Engineers*, and beginning 1947 *Chemical Engineering Progress* (120, East 41st Street, New York 17); *Transactions of the Institution of*  
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## 202 CHEMICAL ENGINEERING—CHEMICAL INTERACTIONS

*Chemical Engineers* (56, Victoria Street, London, S.W.1) ; *Proceedings of the Chemical Engineering Group* of the Society of Chemical Industry (56, Victoria Street, London, S.W.1) ; *Industrial and Engineering Chemistry* (Washington, D.C.), including Annual Reviews in January issues since 1946 ; *Chemical Engineering*, formerly *Chemical and Metallurgical Engineering* (New York) ; *Chemistry and Industry* (London) ; *Chemical Week*, formerly *Chemical Industries* (New York) ; *The Industrial Chemist* (London).

See also Chemical Literature.

**CHEMICAL EQUATIONS** — See Chemical Interactions.

**CHEMICAL EQUIPMENT** — Apparatus that is used on a laboratory or factory scale in chemical processes, frequently as specialized containers, but also in connection with observation and control of such processes. Specially lined factory equipment is discussed in a series of articles in *Ind. Eng. Chem.*, **29**, 373 (Lead-lined) ; 378 (Glass-lined) ; 394 (Rubber-lined) ; 402 (Ceramic-lined) (1937).

**CHEMICAL EQUIVALENT** — See Chemical Compounds.

**CHEMICAL FORMULAS** — See Chemical Compounds.

**CHEMICAL INTERACTIONS (Affinity, Reactions, and Equations)** —

Chemistry is well defined as the study of the laws of the changes or transformations of matter. All articles of food and clothing, building materials, and those needed for decoration or repair, every art and every industry—all depend essentially for their production or conduct upon chemical changes as realized in nature or made by man to serve human purposes. The same is true of the production and decay of animal and vegetable matters, as also the processes by which they are broken up and the resulting products made available in their turn as food for new life ; the very diseases of mankind and animals and their treatment are all chemical in essence and involve chemical changes. These chemical changes constitute a sort of adaptation of matter to environment, and in a sense are acts of creation, as every such change produces new products and liberates or absorbs energy. The new products, although related to the original materials, are quite distinct in character and properties. Thus, in a sense all matter is susceptible to change when the environment is appropriate.

If some broken marble (calcium carbonate) be placed in a dilute solution of hydrochloric acid, a reaction occurs attended with effervescence, due to the escape of carbon dioxide gas, the chemical change that takes place between the marble and the acid being expressed as follows :

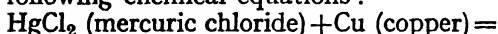
$\text{CaCO}_3$  (calcium carbonate) +  $2\text{HCl}$  (hydrochloric acid) =

$\text{CaCl}_2$  (calcium chloride) +  $\text{H}_2\text{O}$  (water) +  $\text{CO}_2$  (carbon dioxide).

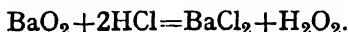
In other words, 1 molecular weight of calcium carbonate and 2 molecular weights of hydrochloric acid produce 1 molecular weight of calcium chloride, 1 molecular weight of water (both of which remain in solution), and 1 molecular weight of gaseous carbon dioxide. In this interaction between a solid body and a liquid, one product is gaseous in character, although it can, in point of fact, be converted

into the liquid state and even made into a solid form like snow by great cooling under pressure. In this equation the symbol Ca represents, on the basis of thorough investigation, 40 *parts by weight* of calcium element, and, similarly, C 12 parts by weight of carbon element, O 16 parts by weight of oxygen element, H 1 part by weight of hydrogen element, and Cl 35.5 parts by weight of chlorine element.

Mercuric chloride is a compound of mercury with chlorine, and if a strip of copper be placed in a slightly acid solution of that substance, a change takes place, causing the mercury to be deposited, and after sufficient time, nothing but copper chloride is found in solution. In other words, the mercury is replaced (owing to the chemical change that takes place) by the copper, and it is found in practice that this exchange takes place in the proportion of 200.6 parts of mercury and 63.6 parts of copper. If this solution of copper chloride be taken afterwards and exposed in turn to the action of a piece of iron, the whole of the copper can be deposited from the solution and replaced by iron; and now it is found that the metals are again exchanged in the ratio of their equivalent weights, 63.6 parts by weight copper being replaced by 55.8 parts by weight iron. These two changes or interactions, it is found upon investigation, can be expressed by the two following chemical equations:



Baryta or barium oxide is represented by the formula BaO, but there is another oxide of barium, known as barium dioxide, which has the formula BaO<sub>2</sub>. Now, when powdered barium dioxide is added to a solution of dilute hydrochloric acid (which has the constitution represented by the formula HCl), exhaustive study has shown that the change which takes place may be represented in the following way, and the symbol Ba represents 137 parts by weight of barium element:



This chemical equation represents the fact that 1 molecule of barium dioxide interacting with 2 molecules of hydrochloric acid (hydrogen chloride) produces 1 molecule of barium chloride and 1 molecule of hydrogen dioxide, both of which, being soluble in water, remain together in solution.

It is further found that the sum of the products is equal to the sum of the substances originally employed, and the equation given above shows that there are *employed* in this chemical interaction:

1 atom or 137 parts by weight of barium	}	As contained in 1 molecule of
2 atoms or 32 " " of oxygen		
2 " " 2 " " of hydrogen	}	As contained in 2 molecules of
2 " " 71 " " of chlorine		

totalling 7 atoms and 242 parts by weight;

and that there are *produced* :

1 atom	or 137 parts by weight	of barium	} As contained in 1 molecule of
2 atoms or 71	" "	of chlorine	
2 " "	2 " "	of hydrogen	} As contained in 1 molecule of
2 " "	32 " "	of oxygen	
totalling 7 atoms and 242 parts by weight.			

In these expressions the terms atom and molecule may well be thought of as being the chemical unit of each substance named therein.

If in the study of any chemical change, the sum of the products found upon analysis is not equal to the sum of the substances employed, it is recognized that the analysis is imperfect. (Law of Conservation of Matter.)

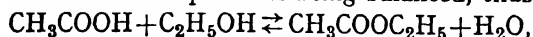
The rate of chemical interaction is proportional to the active masses of the substances involved therein, and several reactions may even take place concurrently on independent lines.

Chemical reactions can occur between substances in the solid states as well as in the gaseous and liquid forms, bringing about, for example, the changes frequently experienced in alloys by heating and cooling, while the fact of diffusion in solids is well established. (See Diffusion.) For example, lead oxide and molybdenum trioxide, as also carbon and silicon, react vigorously at elevated temperatures. It is important to bear in mind that most chemical interactions as experienced in general work are those which take place in the presence of air and exposure to light, both of which factors have a bearing upon many of such chemical changes.

Reaction can often be induced or accelerated by others taking place simultaneously in the same admixtures, or by the use of other substances acting as catalysts or so-called accelerators (see Catalysis, and Rubber), and when they proceed to completion they are termed irreversible, but when they stop short of completion and a consistent equilibrium results they are termed reversible.

The effects of moisture in chemical and physical changes is the subject of a book by J. W. Smith (Longmans, Green and Co., London), who has himself contributed to knowledge of such effects, showing among other things that the removal of moisture causes the stoppage of reaction between sulphur vapour and silver up to about 150° C. (See also Drying (Intensive).)

Reversible or equilibrium or balanced reactions are those in which the products react so that a state of equilibrium is reached, the concentration of factors and products being balanced, thus :



this equation representing both the production of ethyl acetate from acetic acid and ethyl alcohol, and the re-formation of ethyl alcohol and acetic acid at a definite temperature. In other words, at a point measurably short of completion, the velocity of the esterification process is balanced by that of the hydrolysis. Such reactions are common. The complete test of reversibility and equilibrium is attained when the *same* state of affairs exists in the *resulting* system upon using the materials shown *on either side* as the *starting* materials.

The force which brings about chemical combination and keeps the resulting products comparatively intact as entities is correlated to other forms of force, such as heat, light, and electricity. All such changes involve the consumption or expenditure of energy, as was previously mentioned, many being attended by the absorption or emission of heat, of light, or of electricity. A true measure of chemical affinity is the free energy change in chemical interaction, and in many cases this can be calculated. (See Energy.) The energy required in the form of electric current to decompose water into its constituent elements is identical with the energy transformed into heat evolved in the combination of the two gases (hydrogen and oxygen) to form water, when the initial and final systems are identically compared.

Energy changes, involving the use of high and low temperatures, low and high pressures (sometimes to the extent of 50,000 atmospheres), are not shown by chemists as equational changes; equations represent only the materials and the quantities involved.

The generally accepted chemical view is that reaction is attributable to activated molecules possessing a critical increment of energy above the average, as illustrated by the behaviour of activated and nascent forms of chemical entities. The quantity of energy requisite to bring each molecule from its initial to its reactive stage has been termed the "critical increment" characteristic of the specific reaction, and Baly has done much towards the confirmation of this "radiation" theory of chemical reaction. (See *The Kinetics of Chemical Change*, by C. N. Hinshelwood (Oxford Univ. Press); and *Nuclear Chemistry*.)

**CHEMICAL LITERATURE** — See *A Guide to the Literature of Chemistry*, by E. J. Crane and A. M. Patterson (John Wiley and Sons, New York, and Chapman and Hall, London); *Chemical Publications*, by M. G. Mellon (McGraw-Hill Book Co., New York); *Library Guide for the Chemist*, by B. A. Soule (McGraw-Hill Book Co., New York); *A Catalogue of British Scientific and Technical Books*, by Daphne Shaw (A. and F. Denny (1930)); "The Literature of Chemistry and Chemical Engineering," by M. C. Molstad (*Ind. Eng. Chem., News Ed.*, April 10, 1938, pp. 206-214); and *Annual Reports of the Progress of Chemistry* (Chemical Society, London, since 1904); *Annual Reports of the Progress of Applied Chemistry* (Society of Chemical Industry, London, since 1916); *British Abstracts* (Bureau of Abstracts, London, W.1), since 1945, formerly *British Chemical and Physiological Abstracts* (1938-1944) and *British Chemical Abstracts* (to 1937); and *Chemical Abstracts* (American Chemical Society, Washington, D.C., since 1907).

**CHEMICAL PLANT** — The reaction vessels, processing devices, machinery and auxiliary equipment required for the production of chemicals on a large scale. (See Chemical Engineering, and the various unit operations of same.)

*References:* *The Chemical Engineering Catalog* (Reinhold Publishing Corp., New York); *Chemical Industries* (Leonard Hill, Ltd., London). Both are annual publications.

**CHEMICAL REACTIONS** — See Chemical Interactions.

## 206      CHEMICAL SYMBOLS — CHESTNUT EXTRACT

**CHEMICAL SYMBOLS** — See *Frontispiece*, Elements, Chemical Compounds, and Chemical Interactions.

**CHEMICAL TRADE** — See Economic Aspects.

**CHEMICAL WARFARE** — See *Chemical Warfare*, by A. A. Fries and C. J. West (McGraw-Hill Book Co., New York); *Chemicals in War*, by A. M. Prentiss (McGraw-Hill Book Co., New York); and Gassing.

**CHEMICAL WORKS** — See Chemical Plant.

**CHEMOTHERAPY** — The treatment of bacterial infection by means of chemical substances having a specific action against the infecting organism. The ideal chemotherapeutic agent is one which will destroy the infecting organism without having a toxic effect on the cells of the host. Although the ideal has not been achieved, many substances have been introduced into medicine as a result of the study of chemotherapy, *e.g.*, organic compounds of arsenic for the treatment of syphilis, the sulphonamides for the treatment of pneumococcal and other infections, and penicillin. (See *The Chemistry of Drugs*, by G. M. Dyson (Ernest Benn, London); *Recent Advances in Chemotherapy*, by G. M. Findlay (J. and A. Churchill, London); *Chemotherapy, The Extra Pharmacopœia*, Vol. II, 22nd Ed. (1943); *Some Recent Advances in Chemistry in Relation to Medicine*, by D. H. Hey (Royal Institute of Chemistry, London); *The Basis of Chemotherapy*, by T. S. Work and E. Work (Oliver and Boyd, Edinburgh and London); Antiseptics, Bacteria, Biochemistry, Disinfectants, and Toxins.)

**CHENGAL RESIN** — See Penak Resin.

**CHENOPODIUM OIL (Artemisia Oil, Wormseed Oil)** — A yellowish essential oil, distilled from the unexpanded flower-buds of various species of *Artemisia*, including *Artemisia maritima* L. (South Russia and the Levant), *Chenopodium ambrosioides* (U.S.A.) and perhaps *Artemisia annua*, although it has been reported that the botanical source of true wormseed of commerce is *Artemisia cina* (Berg), Willkomm. Chenopodium oil contains from 65 to 70 per cent. of ascaridole, to the presence of which the anthelmintic properties are due; sp. gr. 0.960 to 0.980; ref. ind. 1.474 to 1.479 at 20° C.

The American (Maryland) oil is of sp. gr. 0.9302 to 0.9559, is lævoptatory, contains from 25 to 30 per cent. of mixed hydrocarbons including cymene, and from 60 to 70 per cent. of ascaridole. The Indian oil is said to have a sp. gr. of from 0.908 to 0.940; the Levant oil is said to contain cineole as its chief constituent and to have a sp. gr. of about 0.930. (See Ascaridole, and Santonin.)

**CHERT (HORNSTONE)** — Massive silica (quartz) occurring in limestones of Palæozoic Age and in Mesozoic strata.

**CHESSYLITE** — See Copper (Azurite).

**CHESTNUT EXTRACT** — Prepared by leaching the bark of *Castanea sativa*, containing from 25 to 36 per cent. tannin; used for tanning and in dyeing and calico printing.

**CHIA OIL** — Expressed from the seeds of the Chia plant (*Salvia hispanica*), which grows in Mexico and yields from 24 to nearly 40 per cent.; sp. gr. 0.9338, i.v. 192.2, and sap. v. 192.2. It dries as quickly as linseed oil, which it resembles in odour and taste, is of light amber colour, and is largely used as food and in compounding a particular drink. Further details of its composition are given by Baughman and Jamieson (*B.C.A.*, B, 1929, 902).

**CHICORY** — The root of *Chicorium intybus*, a genus of Compositæ, used when roasted and ground to mix with coffee as an adulterant.

**CHILE NITRE** — See Caliche.

**CHILE SALTPETRE** — See Caliche.

**CHINA (Porcelain, Pottery, Stoneware, etc.)** — Articles made from various classes of minerals, such as China clay (a product resulting from the gradual decomposition of rocks, including *feldspar* and *granite*) in the nature of hydrous aluminium silicates. (See Clays, Porcelain, and Stoneware.)

**CHINA CLAY** — See Clays, and Porcelain.

**CHINA GRASS** — See Ramie.

**CHINA WOOD OIL** — See Tung Oil.

**CHINESE BLUE** — A form of Prussian blue. (See Cyanogen.)

**CHINESE INK** — See Inks.

**CHINESE RED** — Lead Chromate. (See Chrome Yellow, and Lead Chromate.)

**CHINESE WAX** — See Waxes.

**CHINESE WHITE** — Trade name for zinc oxide. (See Zinc Oxide.)

**CHINESE WOOD OIL** — See Tung Oil.

**CHINIOFON** ("Quinoxyl," "Yatren") — A mixture containing one part of sodium bicarbonate and four parts of 7-iodo-8-hydroxyquinoline-5-sulphonic acid. It is a pale yellow, odourless powder; soluble in water with effervescence; insoluble in alcohol, ether, and chloroform. It is used in medicine as an intestinal antiseptic for the treatment of amœbic dysentery.

**CHITIN** — A nitrogen-containing polysaccharide, forming the hard exoskeleton of the crustaceans, insects, and spiders. On acid hydrolysis it yields glucosamine, whereas the enzyme present in the intestine of the snail hydrolyses it to N-acetylglucosamine. Chitin resembles cellulose in some respects, including the fact that the identity period along the fibre axis is 10.4 Ångström units.

**CHLORACETIC ACID** — See Monochloroacetic Acid.

**CHLORACETOPHENONE** ( $\text{Cl} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ ) — Used, mixed with cyanogen chloride, as an exterminant for pests, as the mixture is less dangerous than chloracetophenone used alone.

**CHLORAL** ( $\text{CCl}_3\text{CHO}$ ) — A colourless oily liquid of sp. gr. 1.512 and b.p.  $98.1^\circ\text{C}$ . ; soluble in alcohol and ether ; prepared by the chlorination of absolute alcohol and subsequent treatment of the product with sulphuric acid, followed by distillation. The chloral alcoholate first formed is decomposed by the acid, and upon distillation ethyl chloride comes over first, then alcohol, and finally anhydrous chloral.

**Chloral Hydrate** ( $\text{CCl}_3\text{CH(OH)}_2$ ) is a crystalline body of sp. gr. 1.908, m.p.  $47.4^\circ\text{C}$ ., and b.p.  $97.5^\circ\text{C}$ ., when it dissociates into chloral and water ; prepared from chloral by mixing with a small quantity of water, when heat is evolved. It is readily soluble in water and alcohol, and is again resolved into chloral by the action of sulphuric acid. Used in medicine as a hypnotic and sedative.

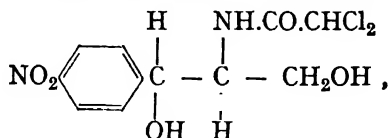
**Chloral Formamide** (Chloralamide) ( $\text{CCl}_3\text{CH(OH).NH.CHO}$ ) is a colourless, odourless, crystalline compound prepared by heating together molecular proportions of chloral and formamide ; slightly soluble in water, soluble in alcohol and ether ; m.p.  $115^\circ\text{C}$ . Used in medicine as a mild hypnotic and sedative.

**Chloral Urethane** ( $\text{CCl}_3\text{3H(OH).NH.COOC}_2\text{H}_5$ ) is the source of a hypnotic known as "Somnal," being a soluble ethyl derivative.

**CHLORAMINE** (Chloramine-T, Tolamine) — A white, crystalline compound, namely, *p*-toluenesulphonchloramide,  $\text{CH}_3\text{.C}_6\text{H}_4\text{.SO}_2\text{Na.NCl.3H}_2\text{O}$  ; obtained from a by-product of the manufacture of saccharin and used as an antiseptic because of its power of slowly liberating chlorine in the presence of organic matter.

**CHLORAMINES** — Derivatives of the sulphonamides, in which one or both of the hydrogens attached to the nitrogen are replaced by chlorine, e.g., Chloramine T. The name is also applied to the chlorine substitution products of ammonia.

**CHLORAMPHENICOL** (Chloromycetin) — A crystalline antibiotic substance, originally isolated from cultures of *Streptomyces* present in a sample of soil from Venezuela. It is a neutral substance containing carbon, hydrogen, nitrogen, and about 22 per cent. of organically combined chlorine. It has been chemically characterized as 2-(dichloroacetylamino)-3-hydroxy-3-(*p*-nitrophenyl)-propanol,



and has been synthesized. It inhibits the growth of a number of Gram-negative organisms, notably, *Brucella abortus*, *Escherichia coli*, *Klebsiella pneumoniae*, *Proteus vulgaris*, *Shigella paradyenteriae* (Sonne), the tubercle bacillus and *Rickettsia prowazeki* (the causative organism of scrub typhus). Chloramphenicol possesses low toxicity and is effective when administered by mouth. It has been tested against experimental infections of scrub typhus in mice and excellent results have been obtained clinically during an outbreak of scrub typhus in Malaya. It

is also used for the treatment of primary atypical pneumonia due to virus infection, infections of the urinary tract due to coliform bacteria and typhoid fever. (See J. Ehrlich *et al.*, *Science*, **106**, 417 (1947); J. E. Smadel and E. B. Jackson, *Science*, **106**, 418 (1947); R. M. Smith *et al.*, *J. Bact.*, **55**, 425 (1948); W. R. Bartz, *J. Biol. Chem.*, **172**, 445 (1948); J. C. Patel, D. D. Banker, and C. J. Modi, *Brit. Med. J.*, **2**, 998 (1949); "Treatment of Epidemic Typhus with Chloromycetin," by E. H. Payne *et al.*, *Trans. Royal Soc. of Tropical Med. and Hygiene*, **42**, No. 2 (Sept., 1948); "The Treatment of Rocky Mountain Spotted Fever with Chloromycetin," by M. C. Pincoffs *et al.*, *Ann. Int. Med.*, **29**, 656 (1948); synthesis of chloramphenicol, *J. Amer. Chem. Soc.*, **71**, 2458 (1949); *Rats, Lice and History*, by Hans Zinsser.)

**CHLORANIL (Tetrachloroquinone)** ( $C_6O_2Cl_4$ ) — A substance prepared by the chlorination of quinone; it crystallizes in yellow plates, and is used as an oxidizing agent in making certain coal-tar dyes, also in a tanning process.

**CHLORANILINES** — Chlorinated derivatives of aniline or mono-amino derivatives of the chlorobenzenes,  $C_6H_4ClNH_2$ ,  $C_6H_3Cl_2NH_2$ , and  $C_6H_2Cl_3NH_2$ .

**CHLORBENZENES** — See Chlorobenzenes.

**CHLORBUTOL ("Chloretone," Chlorobutanol)** ( $CCl_3.C(CH_3)_2OH$ ) — A colourless, crystalline compound, namely, trichloro-*tert.*-butyl alcohol; sparingly soluble in water; soluble in alcohol, ether, and chloroform. It is used in medicine as an antiseptic, and as a sedative and hypnotic in preparations for the prevention of seasickness.

**CHLORDAN(E)** — A chlorinated hydrocarbon insecticide having the formula  $C_{10}H_6Cl_8$ , produced by treating certain coal tar derivatives with chlorine. Sold under the trade names of "Velsicol 1068" and "Octa-Chlor," this material is said to possess qualities similar to D.D.T., and to be superior to the latter against certain insects. (See Kearns *et al.* in *J. Econ. Entomol.*, **38**, 661 (1945); D.D.T., and Insecticides.)

**CHLORETHYLENES** — See Solvents, and Ethylene Dichloride.

"**CHLORETONE**" — See Chlorbutol.

"**CHLOREX**" (UCC) — Trade-mark for solvents used in the refining of petroleum lubricating oils. (See Dichlorodiethyl ether.)

**CHLORGUANIDE** (1-(*p*-chlorophenyl)-5-isopropylbiguanide hydrochloride) — A white powder used as an antimalarial agent. Trade-mark is "Paludrine" (Du Pont).

**CHLORHYDRINS (Halohydrins)** — Organic compounds containing both  $>CCl$  and  $>COH$  groups. (See Dichlorohydrin.)

Monochlorohydrin ( $CH_2Cl.CHOH.CH_2OH$ ) is a yellow thick liquid of sp. gr. 1.325 and b.p.  $128^\circ C.$ , soluble in water and alcohol, made from glycerine and hydrochloric acid.

**CHLORIDE OF LIME** — See Calcium Compounds (Bleaching-Powder), and Chlorine.

**CHLORINATION** — The name given to any process by which chlorine is imported into the constitution of a substance ; for example, lime is converted into bleaching-powder by the action of chlorine, and many additive and substitution products are derived from benzene hydrocarbons by the introduction of chlorine, hydrogen being replaced by chlorine in the last-named instances. Benzene hexachloride ( $C_6H_6Cl_6$ ) is an additive substance produced by exposing benzene to chlorine gas for a prolonged period. Methyl chloride ( $CH_3Cl$ ) illustrates the chlorination act by which hydrogen is replaced by chlorine, and is obtained with other substances when chlorine acts on methane (marsh gas,  $CH_4$ ). In the preparation of benzyl chloride from boiling toluene by the action of chlorine, the following interaction takes place :  $C_6H_5.CH_3 + Cl_2 = C_6H_5.CH_2Cl + HCl$ . The direct chlorination of solid and even powdered organic compounds is often attended with difficulty however good the agitation, by reason of the liability to over-heating

## CHLORINE-CONTAINING SUBSTANCES

## CHART SHOWING PRINCIPAL INTER-RELATIONSHIPS

Arrangement Based on Valency and Reduction-Oxidation Properties  
Arranged by the Editor.

Hydrochloric acid $HCl$	Chlorine $Cl_2$	Hypochlorous acid $HOCl$	Chlorine monoxide $Cl_2O$	Chlorous acid $HOClO_2$	Chlorine dioxide $ClO_2$	Chloric acid $HOClO_3$	Perchloric acid $HOClO_4$	Chlorine heptoxide $Cl_2O_7$
Chlorides INORGANIC Soluble $NaCl$ Reactive with water $PCl_3$ Insoluble $AgCl$		Hypochlorites $NaOCl$		Chlorites $NaClO_2$		Chlorates $KClO_3$		Perchlorates $KClO_4$
<hr/>								
ORGANIC								
1 Cl-atom attached to 1 C-atom :								
Methyl chloride $CH_3Cl$	Ethyl chloride $C_2H_5Cl$	Ethylene dichloride $CH_2Cl$ $CH_2Cl$	Ethylene chlorohydrin $CH_2Cl$ $CH_2OH$	Chloro-benzene $C_6H_5Cl$	Benzyl chloride $C_6H_5CH_2Cl$	Acetyl chloride $CH_3COCl$	Chloroacetic acid $ClCH_2COOH$	
				Dichloro-benzene $C_6H_4Cl_2(1, 4)$				
2 Cl-atoms attached to 1 C-atom :								
Methylene chloride $CH_2Cl_2$	Ethylidene chloride $CH_3CHCl_2$	Acetylene tetrachloride $CHCl_2$ $CHCl_2$	Tetrachloro-ethylene $CCl_2$ $CCl_2$		Benzal chloride $C_6H_5CHCl_2$	Phosgene $COCl_2$	Dichloroacetic acid $Cl_2CHCOOH$	
	Acetone chloride $(CH_3)_2CCl_2$							
3 Cl-atoms attached to 1 C-atom :								
Chloroform $CHCl_3$		Hexachloro-ethane $CCl_3$ $CCl_3$			Benzo tri-chloride $C_6H_5.CCl_3$	Chloral hydrate $CCl_3$ $CH(OH)_2$	Trichloroacetic acid $Cl_3C.COOH$	
4 Cl-atoms attached to 1 C-atom								
Carbon tetra-chloride $CCl_4$								

and irregular penetration, so that when possible it is better to deal with them in a melted state or in a state of solution, the application of heat being in many cases desirable or necessary. The chlorination of indigo in order to obtain monochloroindigo is facilitated by solution in nitrobenzene. The chlorination of phenol can be directed to obtain a series of derivatives, including the ortho-chloro, para-chloro, trichloro, and tetra-chloro compounds.

Hydroxyl groups of alcohols or acids are usually replaced by chlorine by means of phosphorus halides, thus :



A powerful chlorinating agent consists of sulphuryl chloride which may be added to the subject substance previously mixed with a proportion of anhydrous aluminium chloride.

Light, and particularly the ultra-violet radiations, exercise great influence in many processes of chlorination. (See articles on chlorination by H. B. Hass *et al.* in *Ind. Eng. Chem.*, **27**, 1190 (1935) ; **28**, 333 (1936) ; **29**, 1335 (1937) ; *Unit Processes in Organic Chemistry*, by P. H. Groggins (McGraw-Hill Book Co., New York).)

**CHLORINE (Cl) and its Compounds** — Atomic weight, 35.457. See Elements for other data ; and also accompanying Chart. Chlorine is not found in nature in an uncombined state, but exists very extensively in combination with other substances, and most abundantly in the form of common salt—sodium chloride (NaCl). There are large deposits of salt in Cheshire, and it forms part of the well-known Stassfurt saline deposits (in Germany). Combined with hydrogen as hydrochloric acid (HCl), it is a natural constituent of the gastric juice of men and animals. In the form of salt it is always found present in sea-water, thus, the water of the English Channel contains 28.05 parts per 1,000, but in association with other salts common salt (rock salt) is mined to some extent in an impure state in the dry condition, but for the most part (being soluble in water) it is made by pumping water into the salt deposits, and crystallization resulting from evaporation of the brine thus prepared. (See Brine, and Water.)

Chlorine in gaseous form is manufactured on a large scale, and is liquefied for transport and used directly as a sanitary reagent and in the manufacture of many organic and some inorganic chemicals. It was at one time mostly made by the action of hydrochloric acid upon manganese dioxide ores :  $\text{MnO}_2 + 4\text{HCl} = \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2$ . In the Weldon process, the manganese is reprecipitated from the resulting manganese chloride liquor as calcium manganite ( $\text{CaO} \cdot 2\text{MnO}_2$ ) or "Weldon mud," as it is called, by treatment with an excess of milk of lime and oxidation with a current of air at 55° to 60° C., ready for use over again. (See Manganese Oxides.) In the "Deacon" process a mixture of hydrogen chloride (HCl) gas and air is exposed to the catalytic influence of cupric chloride distributed over a widely exposed surface of pumice-stone at a temperature of about 430° C., chlorine

and water being finally produced as follows:  $2\text{HCl} + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O} + \text{Cl}_2$ . This process produces weaker chlorine than the "Weldon" process, but eliminates loss of chlorine as calcium chloride. Both the "Weldon" and the "Deacon" processes have been practically superseded by the electrolytic method of manufacturing chlorine—that is, the direct electrolysis of a concentrated solution of common salt (brine)—in which the gaseous chlorine is evolved at the anode whilst sodium hydroxide and hydrogen are produced at the cathode—a porous diaphragm and a continuous flow of electrolyte generally separate the compartments mechanically and permit the passage of electricity (without a diaphragm the product is sodium hypochlorite by natural or induced mixing of anode and cathode products). Various electrolytic cells are described by C. L. Mantell in *Industrial Electrochemistry* (McGraw-Hill Book Co., New York).

Chlorine gas is greenish in colour, and when sufficiently cooled it freezes to a yellow crystalline mass of m.p.  $-101^\circ\text{C}$ . It immediately passes into the gaseous state when liberated in the air, and has a very violent action on the linings of the mouth, nose, throat, and lungs, causing death when inhaled in serious quantity, the maximum safe concentration being 1 part per million of air. Chlorine is nearly two and a half times heavier than air. It is somewhat soluble in water, 1 volume of which at  $10^\circ\text{C}$ . absorbs 3.1 volumes of chlorine, forming a green solution. When strong chlorine water is cooled to nearly freezing-point, it deposits a crystalline hydrate ( $\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ ) of unstable character. Metallic copper in thin leaf form, metallic antimony in the form of powder, and sodium, all take fire and burn readily in chlorine gas, forming chlorides, although the gas itself is not inflammable. Similarly, a jet of hydrogen gas will burn in a vessel containing chlorine gas, thus producing hydrochloric acid in the form of white fumes which can be absorbed by water, and this process is now employed commercially in the manufacture of hydrochloric acid.

On account of its sterilizing value, chlorine as such, or in the form of bleaching powder, is frequently used for the purification of water supplies, the water of swimming-baths, also that of cooling waters of steam engines and turbines to prevent the growth of living organisms on the inside of the condenser pipes. It is also employed in the manufacture of potassium chlorate, which is extensively used in match-making, and in the preparation of certain explosives, cellulose, rubber substitutes, chloral, chloroform, carbon tetrachloride, and the chlorination of metals and hydrocarbons. (See Chlorination.)

Liquefied chlorine boils at  $-34.6^\circ\text{C}$ . under atmospheric pressure, and is used in the preparation of bleach-liquor, the manufacture of chlorides, dye-intermediates, and non-inflammable solvents.

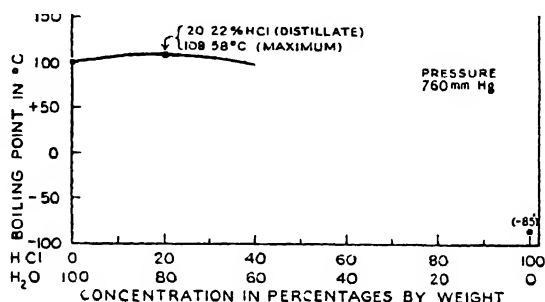
Chlorine can be activated by electrical discharges, by ultra-violet light, and thermally, but the activated gas is unstable above  $50^\circ\text{C}$ . It combines with ozone to form chlorine monoxide: with sulphur to form sulphur monochloride, and with benzene to form  $\text{C}_6\text{H}_5\text{Cl}$ .

**Hydrochloric Acid**, or hydrogen chloride ( $\text{HCl}$ ), is one of the most important compounds of chlorine. The two gases hydrogen and

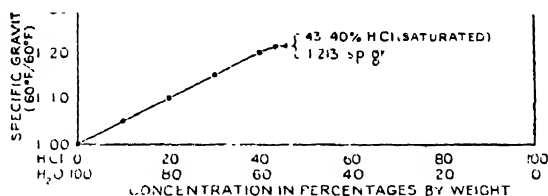
chlorine may be made to combine as described above, but do not combine when mixed together in the dark, although in sunlight or electric light they combine with explosive violence. The acid can be manufactured by the direct combustion method (see *Ind. Chem.*, 6, 489 (1930)) or by the action of strong sulphuric acid upon common salt (in mechanical furnaces which have now replaced the old hand-operated ones) as represented by the equation:  $2\text{NaCl} + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + 2\text{HCl}$ , the acid being distilled over from the mixture in the form of

HCl-H<sub>2</sub>O MIXTURES

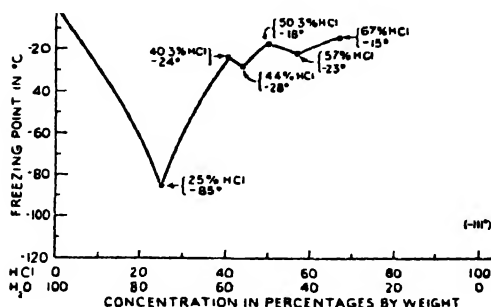
## BOILING POINT—CONCENTRATION RELATIONSHIP

HCl-H<sub>2</sub>O MIXTURES

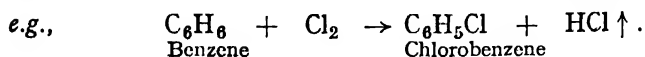
## SPECIFIC GRAVITY—CONCENTRATION RELATIONSHIP

HCl-H<sub>2</sub>O MIXTURES

## FREEZING POINT—CONCENTRATION RELATIONSHIP



gas and absorbed in water, thus furnishing a solution of the acid. Hydrogen chloride is produced when hydrocarbons and chlorine react,



In its gaseous form the acid is colourless, and possesses a pungent, irritating character. It is soluble in water, 1 volume of which at 0° C. and under ordinary atmospheric pressure dissolves 503 volumes. A commercial form known as "Muriatic Tower Salts" is marketed of 28° Tw. strength. The ordinary commercial hydrochloric acid is an aqueous solution of from 28 to 32 per cent. strength, and the synthetic acid now made by the direct combination of hydrogen and chlorine is water white, of great purity, and can be had up to 40 per cent. HCl content. In pure liquefied form it boils at -85° C. under atmospheric pressure.

Hydrochloric acid finds extensive use in the textile, galvanizing, chrome-tanning industries, wire-drawing, metal-etching, soldering, the reduction of aromatic nitrocompounds, and the manufacture of dye-stuffs. It decomposes the oxides and carbonates of the alkaline and other metals, the chloride of the base being produced in each case.

Its storage and transport other than in glass carboys has proved a matter of difficulty, but large wooden vessels lined with soft rubber have been used successfully, and a pitch-binder named "Prodorite" is a good lining material. Ebonite-lined steel tanks are also used for transport, and vessels made of Staffordshire blue-brick cemented together with "Prodorite" can be used for storage.

Several chlorine **oxides** have been reported—viz.,  $\text{Cl}_2\text{O}$ ,  $\text{ClO}_2$ ,  $\text{Cl}_2\text{O}_7$ , and  $\text{ClO}_4$ . (See Oxides.) Chlorine dioxide ( $\text{ClO}_2$ ), unstable and therefore made at the place of use from sodium chlorite ( $\text{NaClO}_2$ ) by reaction with chlorine, is used for the bleaching of flour, for elimination of odour in polluted air, and improvement of taste and destruction of pathogenic organisms in city water supplies.

**Hypochlorous Acid** ( $\text{HOCl}$ ) is only known, apart from its compounds, in association with water, in which it is soluble, the solution being yellowish in colour and having a chlorous odour. It can be made by a number of processes, notably by the action of any dilute mineral acid, such as hydrochloric acid, upon a soluble hypochlorite such as a solution of bleaching-powder. Strong solutions of the acid are unstable and apt to decompose with violence, but dilute ones are more stable and used as powerful oxidizing and bleaching agents.

**Sodium Hypochlorite** ( $\text{NaOCl}$ ) in solution is made by electrolysis of a cold dilute solution of common salt, also by reaction between bleaching-powder and sodium carbonate in solution, or by the direct chlorination of a solution of caustic soda or sodium carbonate. It can be obtained in greenish-yellow, needle-shaped crystalline form by concentration of a solution *in vacuo* at a low temperature; m.p. of  $24.5 \pm 0.5^\circ$ , decomposing below  $25^\circ$ . Several hydrates are known, and that represented by  $\text{NaClO} \cdot \text{H}_2\text{O}$  is liable to explode when warmed or placed in contact

with organic matter. It is used as a sanitary reagent, and more extensively for oxidizing and bleaching purposes. (See "Germicidal Power of Sodium Hypochlorite," by C. K. Johns (*Ind. Eng. Chem.*, **26**, 787 (1934)).)

**Chloric Acid** ( $\text{HClO}_3$ ) can be prepared by the action of dilute sulphuric acid upon barium chlorate, but it is only known in association with water, as a stronger solution than 80 per cent. decomposes upon heating into chlorine and water. It is a powerful oxidant, wood and paper being liable to combustion when a strong solution of it is dropped upon them.

**Perchloric Acid** ( $\text{HClO}_4$ ) can be prepared by the action (under reduced pressure) of strong sulphuric acid upon barium or potassium perchlorate at from  $140^\circ\text{C}$ . and upwards, and, when pure, is a colourless volatile fuming liquid of sp. gr. 1.782 at  $15^\circ\text{C}$ ., possessing very powerful oxidizing properties. Hydrochloric acid can be in large measure converted electrolytically into perchloric acid and perchlorates made therefrom. Many of the perchlorates are soluble bodies. The lead salt is of use for electroplating purposes, the barium and the magnesium perchlorates find use as drying agents. The acid is used as a reagent in the detection of potassium salts, potassium perchlorate being precipitated.

**Chlorine trifluoride** ( $\text{ClF}_3$ ) has been prepared, by the action of chlorine on hydrogen fluoride at the temperature of liquid air, as a colourless gas which condenses to a pale green liquid of b.p.  $11^\circ\text{C}$ .; the solid form is colourless and of m.p.  $-83^\circ\text{C}$ . **Chlorine monofluoride** ( $\text{ClF}$ ) is also known as a gas of low b.p. ( $-101^\circ\text{C}$ .), and is exceedingly reactive with metals. **Iodine monochloride** ( $\text{ICl}$ ) is a liquid resembling bromine, and formed by interaction of chlorine and iodine.

**CHLORITE (Ripidolite)** — A mineral, hydrated double silicate of aluminium and magnesium coloured green with iron, often found in association with garnet, quartz, and calcite; crystal systems Nos. 3 and 5, and sp. gr. 2.6 to 2.8. A white chlorite from Madagascar has a composition approximating to  $3\text{Al}_2\text{O}_3, 12\text{MgO}, 7\text{SiO}_2, 10\text{H}_2\text{O}$  (J. Orcel).

**CHLOROBENZENES (Chlorobenzenes)** — Most of the chlorinated derivatives can be obtained in succession up to  $\text{C}_6\text{Cl}_6$ . The mono-compound  $\text{C}_6\text{H}_5\text{Cl}$  is obtained by direct action of chlorine upon benzene in presence of aluminium-mercury couple acting as a carrier or in the presence of molybdenum chloride. This liquid has a sp. gr. 1.107 and b.p.  $132^\circ\text{C}$ ., is soluble in alcohol and ether, and is used in the dyestuffs industry, and in the manufacture of picric acid. The ortho- and para-dichlorobenzenes are used as solvents and in preparing dichloranilines; the para isomer is used as a pest destroyer in horticulture.

**CHLOROBUTANOL** — See Chlorbutol.

**CHLOROCRESOL** (*para-Chloro-meta-cresol*) ( $\text{C}_7\text{H}_7\text{OCl}$ ) — A colourless, crystalline compound, namely, 6-chloro-3-hydroxytoluene, prepared by chlorinating *m*-cresol; sparingly soluble in water; soluble in alcohol and ether; m.p.  $64^\circ$  to  $66^\circ\text{C}$ . It has a characteristic odour; used in pharmacy as a preservative in solutions for parenteral administration. (See H. Berry on "The Activity of Chlorocresol Against

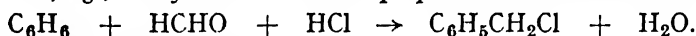
Spores of *Bacillus Subtilis* " in *Quart. J. Pharm.*, **11**, 728 (1938) ; Wien on the toxicity of chlorocresol in *Quart. J. Pharm.*, **12**, 212 (1939) ; J. W. Hadgraft and P. Short on " The Compatibility of Chlorocresol " in *Pharm. J.*, **1**, 202 (1947).)

**CHLOROFORM** ( $\text{CHCl}_3$ ) — A colourless, volatile liquid prepared by the action of chloride of lime and water on acetone or alcohol, followed by distillation. On exposure to light and air, it may be decomposed with the formation of carbonyl chloride (phosgene) and, for medicinal purposes, 2 per cent. of ethyl alcohol is added to chloroform to prevent this decomposition. Chloroform possesses a characteristic odour and sweet, burning taste, b.p.  $61.2^\circ \text{C.}$ , sp. gr. 1.489. It is used as an anaesthetic agent but has now largely been replaced by less toxic substances. Technical grades are used as solvents in industry.

**CHLOROGUANIDE HYDROCHLORIDE** — See Proguanil Hydrochloride.

**CHLOROMETHANE** — See Methyl Chloride.

**CHLOROMETHYLATION** — The introduction of the group  $-\text{CH}_2\text{Cl}$  into an aromatic compound by the action of formaldehyde and hydrochloric acid gas in the presence of a catalyst, such as zinc chloride or aluminium chloride, *e.g.*, benzyl chloride can be prepared from benzene as follows :



**CHLOROMYCETIN** — See Chloramphenicol.

**CHLORONOME** — An apparatus for the use of chlorine gas from cylinders.

**CHLOROPHENOLS** — *o*- and *p*-Chlorophenols are formed by action of chlorine upon phenol, and the *m*- compound by reduction and diazotization of the haloid nitrobenzenes ; all the five hydrogen atoms of phenol can be replaced by chlorine (and bromine). *p*-Chlorophenol is colourless, crystalline, m.p.  $42^\circ \text{C.}$ , and b.p.  $217^\circ \text{C.}$  The *m*- compound is also crystalline, m.p.  $33^\circ \text{C.}$  and b.p.  $214^\circ \text{C.}$ , while the *o*- compound is a colourless oil of m.p.  $7^\circ \text{C.}$  and b.p.  $175^\circ \text{C.}$

**CHLOROPHENOTHANE** — See D.D.T.

**CHLOROPHYLL** — Green plants contain at least two green pigments, by means of which they are able to synthesize carbohydrates. These are designated as chlorophyll a ( $\text{C}_{55}\text{H}_{72}\text{N}_4\text{O}_5\text{Mg}$ ) and chlorophyll b ( $\text{C}_{55}\text{H}_{70}\text{N}_4\text{O}_6\text{Mg}$ ). Both of these absorb light of all wave lengths, with maximum absorption in the blue-violet and red portions of the spectrum. The chlorophyll content of green leaves varies with the plant species, but usually is in the neighbourhood of 1 per cent. of the dry weight. By means of chlorophyll (and possibly other plant pigments) the energy of sunlight is utilized to synthesize carbohydrates from carbon dioxide and water : the reaction is a complex one. Chlorophyll has the property of deodorizing air, and is used for "purifying" air in rooms and for destroying odour of breath. (See *Photosynthesis and Related Processes*, by E. I. Rabinowitch (Interscience Publishers, New York) ; *Photosynthesis*, by Spoehr (Reinhold Publishing Corp., New York) ; also Photocatalysis, Plant Colouring Matters, and Plant Life.)

**CHLOROPICRIN** ( $\text{CCl}_3\text{NO}_2$ ) — A heavy suffocating liquid, made from picric acid by the action of bleaching-powder or chlorine. It was used as a poison gas in World War I, and has been applied as a fumigant for cereal products and for killing silkworm cocoons and mill and household insects when mixed with an equal volume of carbon tetrachloride and applied by an atomizer. With iron filings and acetic acid, it is reduced to methylamine.

**CHLOROPLASTS** — See Plant Colouring Matters.

**CHLOROQUINE DIPHOSPHATE** ( $\text{C}_{18}\text{H}_{32}\text{O}_8\text{N}_3\text{ClP}_2$ ) — A white, crystalline compound, namely, 7-chloro-4-(diethylamino-1-methylbutylamino)-quinoline diphosphate, soluble in water; insoluble in alcohol, benzene, chloroform and ether. It exists in two forms; one melting between  $193^\circ$  and  $195^\circ\text{C}$ ., the other between  $215^\circ$  and  $218^\circ\text{C}$ . It is used for the treatment of malaria, showing a high activity against the erythrocytic forms of *Plasmodium vivax* and *P. falciparum* but it is of no value as a prophylactic. For a review of the chemotherapy of drugs used in the treatment of malaria, see N. Hamilton Fairley in *Brit. Med. J.*, **2**, 891 (1949). (See Mepacrine Hydrochloride, Pamaquin, and Proguanil Hydrochloride.)

**CHLOROSULPHONIC ACID** ( $\text{SO}_2(\text{OH})\text{Cl}$ ) — A brown, oily, corrosive liquid sp. gr. 1.784, soluble in water, made by action of chlorine on cooled sulphuric acid. Used in making saccharin, and smoke screens.

**CHLOROXYLENOL** (*para-Chlor-meta-xyleneol*) ( $\text{C}_6\text{H}_3(\text{CH}_3)_2(1,3)\text{OH}(5)\text{Cl}(2)$ ) — A slightly off-white crystalline compound obtained by reaction between xylenol and sulphuryl chloride; sparingly soluble in water; soluble in alcohol, ether, and benzene; m.p.  $114^\circ$  to  $116^\circ\text{C}$ . It is extensively used as an antiseptic and disinfectant, being the active constituent of a number of proprietary antiseptic solutions such as "Dettol."

**CHOCOLATE** — See Cacao.

**CHOKE-DAMP** (**Black-Damp**) — A mixture of carbon dioxide and other poisonous gases met with in coal-workings, particularly after explosions.

**CHOLESTEROL** (**Cholesterine**) ( $\text{C}_{27}\text{H}_{45}\text{OH}$ ) — Occurs naturally in all tissues of the animal body, especially the spinal cord and brain. Gall stones consist very largely of cholesterol. The spinal cords of cattle are the main commercial source. It was once thought to be a precursor of vitamin D, but it has been found that pure cholesterol does not develop any antirachitic activity on irradiation, a property of the impurities difficult to remove. When recrystallized from alcohol it occurs as white, pearly plates. It is insoluble in water, but soluble in ether and alcohol, and melts at  $148^\circ\text{C}$ . It is a secondary alcohol and the molecule contains one double bond and four rings, being a derivative of cyclo-pentenophenanthrene. It is only one of a very large number of naturally occurring derivatives of this hydrocarbon. (See Sterols, and Vitamins.)

**CHOLIC ACID** — See Taurocholic Acid, and Bile.

**CHOLINE** ( $C_5H_{15}O_2N$ ) — A basic substance obtainable from brain-matter and bile which yields muscarine under certain conditions of oxidation. (See Acetylcholine, and Vitamins.)

**CHONDRUS** — See Sea-weeds.

**CHROMATES** — See Chromium Compounds, and Chrome Yellows.

**CHROMATOGRAPHIC ADSORPTION** — When a solution containing several solutes is poured down a long column packed with such a material as finely powdered alumina, magnesium oxide, or charcoal, the solid will adsorb to varying degrees the different constituents of the mixture in solution. The material taken up by the upper layers of solid will consist largely of the solute that is most readily adsorbed. Other constituents will be gradually adsorbed as they pass further down the packed column. In this way a partial separation of constituents can be accomplished, with the most strongly adsorbed substance at the top and successive layers of the other solutes in order of their ease of adsorption.

The process as above described can occur with coloured and non-coloured solutes. Many of the early separations of this type were made with solutes having distinguishing colours, and hence the adsorption layers in the packed column appeared as a series of coloured bands and thus the process derived the name "chromatographic adsorption." The term is now used for the process whether or not there is colour associated with the adsorption bands. After completion of the separation the column of solid is removed from the tube and cut up into sections from which the concentrated solute may be extracted. The individual layers can be readily seen if coloured, in other cases some other physical phenomenon must be utilized to separate the various layers, such as behaviour to ultra-violet or infra-red light.

*References* : "Chromatography," by Harold H. Strain, *Anal. Chem.*, **22**, 41 (1950); "Paper Chromatography," by Doris Clegg, *Anal. Chem.*, **22**, 48 (1950); *Chromatographic Adsorption Analysis*, by H. H. Strain (Interscience Publishers, New York); *Principles and Practice of Chromatography*, by Zechmeister and Chelnoky (John Wiley and Sons, New York).

**CHROME ALUM** — See Alum (Chrome).

**CHROME GREEN** — Trade name for chromium oxide ( $Cr_2O_3$ ) ; used also in respect of a mixture of Prussian blue and lead chromate.

**CHROME IRON ORE (Chromite)** — See Chromium.

**CHROME RED** — Also known as "American Vermilion," "Persian Red," and "Derby Red," has the composition of the basic character represented by  $Pb_2CrO_6$ , and results from interaction between lead chromate with sodium hydroxide or normal potassium chromate and lead chromate ; or, again, by precipitation of lead chromate in presence of excess of basic lead acetate followed by heating.

**CHROME SALT-CAKE** — An impure yellowish or greenish sodium sulphate obtained as a by-product in making potassium dichromate.

**CHROME YELLOWS** — Essentially lead chromate ( $\text{PbCrO}_4$ ). They can be prepared from a solution of a chromate and one of a lead salt, and are classed as "Chinese Red," "Acetate Chrome," "Chloride Chrome," "Nitrate Chrome," and so forth. They vary greatly in shade (from bright citron yellow to orange), in bulk (density), and oil absorptive power. The lighter shades are made by addition of small proportions of sulphuric, tartaric, or citric acid, and the darker ones by that of caustic soda, to the normal chrome, which is the palest pure middle chrome. The zinc chromes are paler and more permanent to light, but of less covering power.

**"CHROMETAN"** — See Tanning.

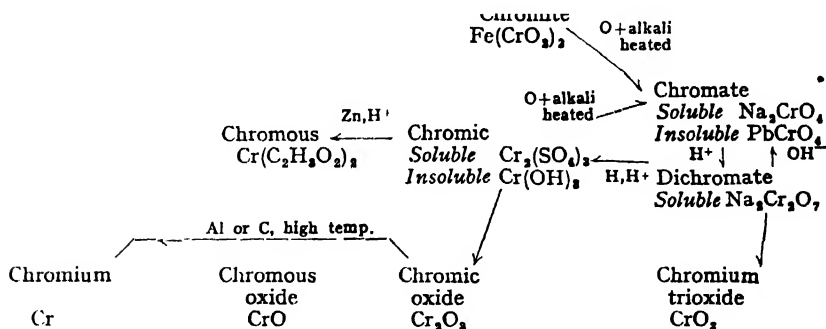
**CHROMIC ACID** — See Chromium Compounds.

**CHROMITE** — A mineral of mixed oxides of iron and chromium, of crystal system No. 1, and sp. gr. 4.3 to 4.6. In the pure form as  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ , it is stated to occur only in meteorites, the mineral forms varying in composition in respect of the two oxides. (See Chromium.)

### CHROMIUM-CONTAINING SUBSTANCES

#### CHART SHOWING PRINCIPAL INTER-RELATIONSHIPS

Arrangement Based on Valency and Reduction-Oxidation Properties.  
Arranged by the Editor.



**CHROMIUM (Cr) and its Compounds** — Atomic weight, 52.01. See Elements for other data; and also accompanying Chart. Chromium occurs in nature in combination in a number of minerals, including chrome iron ore or *chromite* ( $\text{Cr}_2\text{O}_3 \cdot \text{FeO}$ )—the main source from which chromium and its compounds are made, and which yields from 48 to 53 per cent. of the oxide. Large supplies come from Asia Minor, Greece, India, Russia, New Caledonia, U.S.A., Canada, and in particular from Rhodesia, while potential sources are known in California and Oregon (U.S.A.), in Portuguese Africa, in French Oceania, and in Cuba. Chromium also occurs in the forms of lead chromate or *crocoite* ( $\text{PbCrO}_4$ ) and *chrome ochre* ( $\text{Cr}_2\text{O}_3$ ). Chromite is used, among other applications, in the manufacture of chromite bricks for lining metallurgical furnaces.

dichromate and potassium chloride, followed by crystallization, and is used in photography and the tanning industry.

**Sodium Chromate** ( $\text{Na}_2\text{CrO}_4 \cdot 10\text{H}_2\text{O}$ ) is a yellow efflorescent salt, m.p.  $20^\circ \text{C.}$ , soluble in water, used in ink-making, tanning, and dyeing, made as stated under Sodium Dichromate. Sodium peroxide is used commercially to oxidize chromium salts (such as chromic oxide) into chromates by fusion.

**Sodium Dichromate** ( $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), a yellow crystalline salt, soluble in water, is manufactured by fluxing chrome iron ore with lime and soda ash, and conversion of the sodium chromate so obtained, by the action of sulphuric acid, followed by crystallization ( $2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{Cr}_2\text{O}_7 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$ ). It is cheaper than the corresponding potassium compound, but has the disadvantage of being very hygroscopic. It is used industrially for the same applications as the potassium salt, and the ammonium dichromate is used as a mordant for dyeing.

**Chromium Chloride** ( $\text{CrCl}_3$ ) — A nearly insoluble, violet, crystalline body; its hydrate ( $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ ) is green, soluble in water, and used as a mordant.

**Chromium Phosphate** ( $\text{CrPO}_4$ ) (Plessy's green) is insoluble in water and used as a pigment.

**Chromium Sulphate** ( $\text{Cr}_2(\text{SO}_4)_3$ ) and its hydrate ( $\text{Cr}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ), the former being insoluble, but the latter soluble in water, are both used in the textile trades.

**Chromium Potassium Sulphate** ( $\text{K}_2\text{SO}_4 \cdot \text{Cr}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ ) is a violet-red crystalline salt, soluble in water, used as a chrome tan liquor and in the textile industry. (See Alum Chrome.)

**Chromium Fluoride** ( $\text{CrF}_3 \cdot 4\text{H}_2\text{O}$ ) is a green crystalline substance used as a printing, dyeing, and colouring material.

**Chromium Borate** is used as a pigment in calico printing.

**Chromium Acetate** ( $\text{Cr}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot \text{H}_2\text{O}$ ) is a greenish powder soluble in water, used in dyeing and calico printing.

**Chromium Formate**, made by interaction between sodium dichromate, sodium disulphite, and formic acid, is used in the calico-printing industry.

Other chromium compounds include **chromous chloride** ( $\text{CrCl}_2$ ) and **chromous sulphate** ( $\text{CrSO}_4 \cdot 7\text{H}_2\text{O}$ ), several hydroxides, one of which —**chromic hydroxide** ( $\text{Cr}(\text{OH})_3$ ) — is obtained as a gelatinous precipitate by adding sodium, potassium, or ammonium hydroxide solution to a chromium salt solution. (See Tanning.)

**CHROMOGENS** — The parent compounds of dyestuffs, into which they may be converted by the addition of auxochromes, such as  $-\text{NH}_2$ , or  $-\text{SO}_2\text{OH}$ . (See Auxochromes, Chromophores, and Dyes.)

**CHROMOPHORES** — The particular atomic groupings characteristic of coloured organic compounds, such as  $-\text{N}:\text{N}-$  and  $-\text{NO}_2$ , for example, azobenzene ( $\text{C}_6\text{H}_5 \cdot \text{N}:\text{N} \cdot \text{C}_6\text{H}_5$ ), which is a chromogen containing the chromophore  $-\text{N}:\text{N}-$ . (See Chromogens, and Dyes.)

**CHROMOPLASTS** — The chromo-coloured matters in plant cells. (See Plant Colouring Matters.)

**CHRYSAMINE** — A substantive yellow coal-tar dye of the "Congo" class used in the leather and textile trades; prepared from salicylic acid and benzidine.

**CHRYSAROBIN** — A mixture of substances, consisting mainly of chrysophanolanthranol ( $C_{15}H_{12}O_3$ ), chrysophanol or chrysophanic acid ( $C_{15}H_{10}O_4$ ), and emodin monomethyl ether; obtained by extraction with hot benzene from *Araroba* (Goa powder) deposited in the wood of *Andira Araroba*. It is insoluble in water, slightly soluble in alcohol, soluble in hot chloroform and in hot benzene. Chrysarobin is incorporated in ointments for the treatment of psoriasis and ringworm of the scalp.

**CHRYSAZIN (1, 8-Dihydroxyanthraquinone)** ( $C_{14}H_6O_2(OH)_2$ ) — A reddish-brown, crystalline body, m.p.  $191^{\circ}C.$ ; soluble in alcohol; used in dyestuffs.

**CHRYSENE** ( $C_{18}H_{12}$ ) — A white, crystalline hydrocarbon, m.p.  $251^{\circ}C.$ , b.p.  $448^{\circ}C.$ , contained in the coal-tar distillate which comes over above  $360^{\circ}C.$ , resembling anthracene in general properties.

**CHRYSOBERYL** — A mineral gem, of crystal system No. 4, and sp. gr. 3.5 to 3.8, consisting of the oxides of aluminium and beryllium ( $Al_2O_3, BeO$ ).

**CHRYSOIDINE** — An orange-red colouring matter which dyes silk and wool directly. It is a hydrochloride of 2,4-diaminoazobenzene ( $C_6H_5.N : N.C_6H_3(NH_2)_2.HCl$ ), slightly soluble in water.

**CHRYSOLITE** — See Olivine.

**CHRYSOPHANIC ACID** — See Chrysarobin.

**CHRYSOPRASE** — A variety of chalcedony.

**CHRYSOTILE** — A fibrous, silky variety of the mineral serpentine, and a kind of asbestos (see same). Chrysotile is the term used by U.S. Bureau of Mines for asbestos. (See Olivine.)

**CHYLE** — The digested alkaline fluid resulting from the conversion of chyme by action of the biliary and pancreatic juices, and thus prepared ready for absorption by the lacteals of the intestines for conversion into blood.

**CHYME** — The stomach-digested food before it is acted upon by the bile and pancreatic juice.

**CIDER** — Fresh or fermented juice of apples. In American usage, *cider* refers to unfermented apple juice; *hard cider* to fermented juice. In European countries *cider* refers to the fermented juice containing from 5 to 9 per cent. alcohol. For grade designations and characteristics see Agricultural Produce Grading and Marketing Act, 1928 (H.M. Stationery Office).

**" CIMENT FONDU "** — See Cement.

**CIMOLITE** — A mineral hydrous aluminium silicate occurring in the island of Argentiera, Bohemia, and Russia ; of sp. gr. 2.18 to 2.30, used as an absorbent. (See Fuller's Earth.)

**CINCHOCAINE HYDROCHLORIDE** ("Nupercaine") ( $C_{20}H_{29}O_2N_3 \cdot HCl$ )

— A white, hygroscopic, crystalline substance, being the hydrochloride of the  $\beta$ -diethylaminoethylamide of 2-butoxycinchoninic acid ; soluble in water, alcohol, acetone, and chloroform. Used in medicine as a local and spinal anæsthetic.

**CINCHONA** (Red Cinchona Bark, Jesuit's Bark, Loxa Bark, Peruvian Bark) — The dried bark of *Cinchona Calisaya*, *C. Ledgeriana*, *C. officinalis*, *C. succirubra*, and other species of *Cinchona*, which are indigenous to South America and cultivated in Java, Ceylon, and India. Cinchona contains from 5 to 10 per cent. of total alkaloids, the most important of which are quinine (about 3 per cent.), cinchonine, quinidine, and cinchonidine. In all, there are about twenty different alkaloids which occur in the bark in combination with cinchotannic, quinovic, quinic, and oxalic acids. Cinchona is used in medicine in the form of extracts and tinctures and the exhausted bark is used in the tanning industry. (See Keenan and Warren, on the separation of the alkaloids, in *J. Amer. Pharm. Ass.*, **34**, 300 (1945) ; and Quinoline.)

**Quinine** ( $C_{20}H_{24}O_2N_2 \cdot 3H_2O$ ) is a white, crystalline alkaloid of m.p.  $67^\circ C.$ , m.p. of the anhydrous form  $175^\circ C.$  ; slightly soluble in water, soluble in alcohol, chloroform, and ether. The total synthesis of quinine was effected in 1944 by Doering and Woodward, but commercially the alkaloid is obtained by extraction from Cinchona Bark. One method of extraction consists in mixing the finely ground bark with powdered lime, extracting the mixture with hot high-boiling paraffin oil and, after filtration, shaking the filtrate with dilute sulphuric acid. The acid solution is then neutralized with sodium carbonate solution and, upon cooling, the quinine sulphate crystallizes out, and from this the alkaloid can be obtained by treatment with a solution of ammonium hydroxide. Quinine is used in medicine in the form of its sulphate or hydrochloride for the treatment of malaria and as an antipyretic and bitter tonic. Quinine sulphate ( $(C_{20}H_{24}O_2N_2)_2 \cdot H_2SO_4$ ) is a white crystalline powder having a bitter taste ; soluble in water (1 in 350) ; solutions exhibit a strong fluorescence. (See Woodward and Doering, in *J. Amer. Chem. Soc.*, **66**, 849 (1944) ; **67**, 860 (1945).)

**Cinchonine** ( $C_{19}H_{22}ON_2$ ) is a white crystalline alkaloid, slightly soluble in alcohol and ether, m.p.  $264^\circ C.$  The hydrochloride, nitrate, and sulphate are all soluble in water. Cinchonine sulphate ( $(C_{19}H_{22}ON_2)_2 \cdot H_2SO_4$ ) is used as a reagent for the determination of tannin in various materials.

**Cinchonidine** ( $C_{19}H_{22}ON_2$ ) is a white crystalline alkaloid, soluble in alcohol, m.p.  $207^\circ C.$

**Quinidine** ( $C_{20}H_{24}O_2N_2$ ) is a white crystalline alkaloid, soluble in alcohol and ether, m.p.  $171.5^\circ C.$  It is stereoisomeric with quinine.

In the form of its sulphate, quinidine is used in medicine for the treatment of cardiac arrhythmia.

**Totaquine** is a mixture of alkaloids obtained from the bark of various species of *Cinchona* and contains not less than 70 per cent. of total alkaloids of which not less than one-fifth is quinine. It is used for the treatment of malaria, but possesses no therapeutic advantages over quinine except that it is cheaper.

**CINCHOPHEN** ("Atophan," Quinophan) ( $C_{16}H_{11}O_2N$ ) — A white or yellowish, crystalline compound, namely, 2-phenylquinoline-4-carboxylic acid, obtained by interaction between pyruvic acid and benzyldenedeaniline; insoluble in water, slightly soluble in alcohol and ether; sparingly soluble in chloroform; m.p.  $213^{\circ}$  to  $216^{\circ}$  C. It is used in medicine as a remedy for gout and certain types of arthritis.

**CINEOLE** (Cineol, Eucalyptol) ( $C_{10}H_{18}O$ ) — The chief constituent of oil of eucalyptus and present in many other essential oils. It is derived from terpene hydrate ( $C_{10}H_{22}O_3$ ) by dehydration, and is the anhydride of menthan-1,8-diol; a colourless liquid of characteristic camphoraceous odour; soluble in ether; sp. gr. 0.928 to 0.930; ref. ind. 1.456 to 1.460 at  $20^{\circ}$  C.; b.p. about  $176^{\circ}$  C.

**CINNABAR** — Native sulphide of mercury (HgS), of crystal system No. 3, and sp. gr. about 9.0; used as a pigment; mines are located in Spain, California, Germany, China, Japan, and elsewhere. (See Mercury.)

**CINNAMIC ACID** ( $C_6H_5.CH : CH.CO_2H$ ) — A white, crystalline derivative of benzene found present in Peru and Tolu balsams, and liquid storax. It can be prepared by refluxing at  $180^{\circ}$  C. for 8 hours a mixture of benzaldehyde, acetic anhydride, and anhydrous sodium acetate (Perkin). It is soluble in alcohol, ether, and hot water, and yields benzoic acid upon oxidation; when fused with potash, it splits up into benzoic and acetic acids; is monobasic; m.p.  $133^{\circ}$  C., b.p.  $300^{\circ}$  C.; forms a large variety of crystallizable salts, and is used in perfumery. (See Balsams (Storax).)

**CINNAMIC ALCOHOL** (Styrone or Cinnamyl Alcohol) ( $C_6H_5.CH : CH.CH_2OH$ ) crystallizes in white needles, is soluble in alcohol and ether, has an odour like that of hyacinths, and is used in perfumery. It occurs as cinnamic ester (styracin, cinnamyl cinnamate) in storax, and is prepared from that substance by the action of potassium hydroxide, followed by distillation. It can also be prepared from cassia oil. Its sp. gr. is 1.0397 and b.p.  $257^{\circ}$  C. By oxidation it yields cinnamic acid, and when the oxidation is more vigorous, benzoic acid. (See Balsams, Cassia Oil, Storax, and Styrene.)

**CINNAMIC ALDEHYDE** ( $C_6H_5.CH : CH.CHO$ ) — An aromatic oily body of sp. gr. 1.040, ref. ind. 1.6195, m.p.  $33^{\circ}$  C., and b.p.  $254^{\circ}$  C., forming the chief constituent of cinnamon oil (from *Cinnamomum zeylanicum*) in which it occurs to the extent of about 58 per cent.; miscible with alcohol and ether. Used in perfumery and medicine.

**CINNAMON** (Ceylon Cinnamon) — The dried inner bark of the shoots of coppiced trees of *Cinnamomum zeylanicum*. It yields from about 1 to K.C.E.—8

2 per cent. of volatile oil, obtained from the bark by distillation with salt water and which contains about 58 per cent. of cinnamic aldehyde and 4 to 8 per cent. of eugenol. The oil possesses an aromatic pleasant odour and taste, and is used in perfumery, also for flavouring and in medicine as a carminative. It is soluble in alcohol and ether; sp. gr. 1.000 to 1.030 at 15.5° C., ref. ind. 1.565 to 1.582 at 20° C.; specific rotation 0° to -1°. Inferior barks, obtained from other species of *Cinnamomum* come from Java, Brazil, South India, and the West Indies.

Cinnamon leaf oil is distilled from the leaves of the *Cinnamomum zeylanicum*, the yield being from 1.5 to 2 per cent. It is pale yellow, has a characteristic spicy odour, contains from 70 to 75 per cent. eugenol and about 3 per cent. cinnamic aldehyde; sp. gr. 0.995 to 1.044 at 20° C., ref. ind. 1.535 at 20° C., opt. rot. 0° 5' to -1°. The oil is used as a source of eugenol for the synthesis of vanillin. (See Cassia Oil, and Vanilla.)

**CITRAL** (or **Geranial**) ( $C_{10}H_{16}O$ ) — An aldehyde of the terpene series, stated to consist of *cis*- and *trans*-isomerides, found in the oils of lemon (about 5 per cent.), orange, verbena, and lemon-grass (from 70 to 80 per cent.). It is a colourless oil, used in perfumery, and as a source of ionone; it boils at 119° C. (2 mm.); may be obtained by the oxidation of geraniol, which is its corresponding alcohol ( $C_{10}H_{18}O$ ), and forms the chief constituent of Indian geranium oil. (See Geraniol, and Irone.)

**CITRENE** — See Terpenes.

**CITRIC ACID** ( $COOH.CH_2.C(OH)(COOH).CH_2.COOH$ ) — Occurs naturally in many fruits, including tomatoes, pineapples, lemons, citrons, oranges, red bilberries, strawberries, raspberries, and in association with malic acid in gooseberries. It is industrially prepared from juice of the *Citrus medica* and other citrous order fruits, being mainly produced in Sicily and adjacent Italian mainland provinces, and in California (U.S.A.). It is also found as calcium citrate in potatoes, beetroot, etc., but lemon-juice and lime-juice are the materials from which it is usually made. Certain enzymes are capable of building up the acid in citrous fruits, and it is stated to be produced by the action of *Aspergillus fumigatus* on 15 per cent. solutions of calcium gluconate. (See Glucose.)

In a direct process worked out by C. Crotto, the lemon-juice is concentrated to the consistency of a paste and then macerated with acetone of twice its weight, after which it is filtered from the albuminous and other insoluble material and the filtrate mixed with half its weight of distilled water, in which the citric acid dissolves, while the acetone is separated and recovered. It is now manufactured on an extensive scale in the U.S.A. by the fermentation of sucrose solution or molasses containing some nutrient salts, using the spores of a special strain of the mould *Aspergillus niger*. The citric acid can be precipitated as calcium or barium citrate and the acid worked up from the product. F. J. Cahn (*Ind. Eng. Chem.*, 27, 201

(1935)) describes the production of citric acid by this process and claims to obtain a yield of 45 per cent. of the sugar content of molasses, and 55 per cent. on pure sucrose. The fermentation period is from 38 to 60 hours on such materials as beet pulp and cane pulp.

When pure, citric acid crystallizes in association with water ( $C_6H_8O_7 \cdot H_2O$ ) in large, colourless, rhombic prisms, of m.p.  $153^\circ C$ . readily soluble in water. Citric acid and its salts are used in the preparation of summer drinks, in medicine, and extensively in dyeing and calico printing; although formerly used as a remedy for scurvy, citric acid is useless for this purpose, the antiscorbutic properties of lemon juice being due to the vitamin C content.

**Citrates of the alkalis** are soluble in water, and sodium citrate is used in blood transfusions, as it prevents the blood clotting prior to its introduction into the patient.

**Calcium citrate** is insoluble in water and is used in the purification of citric acid.

**Iron and ammonium citrate** is a tonic, used in medicine and prepared by dissolving freshly prepared ferric hydroxide in citric acid solution, neutralizing with ammonia, and evaporating to a scaly solid.

**Iron and quinine citrate** is similar to the above but contains quinine, and is used for the same purpose.

**Citrate of magnesia** is an effervescent medicinal preparation containing magnesium sulphate granulated with sodium bicarbonate and citric acid, the two latter ingredients causing the "fizz" when the substance is added to water.

**CITRON (CEDRAT) OIL**, from *Citrus medica* (peel), contains 5 to 6 per cent. citral, together with limonene and dipentene, has a sp. gr. of  $0.851$  at  $15^\circ C$ ., opt. rot.  $+67^\circ$  to  $+80^\circ$  at  $20^\circ C$ ., and ref. ind.  $1.475$  at  $20^\circ C$ . The fruit is used in perfumery and for making candied peel.

**CITRONELLA OIL (Lana Batu)**—A limpid, pale yellow, essential oil distilled from the grass, *Cymbopogon Nardus*, which yields from 0.5 to 1 per cent. Two types of oil are known in commerce, namely Ceylon and Java. Java oil contains from 30 to 40 per cent. of citronellal together with geraniol and methyleugenol; sp. gr.  $0.885$  to  $0.900$  at  $15^\circ C$ ., opt. rot.  $-2^\circ$  to  $-5^\circ$ , ref. ind.  $1.468$  to  $1.473$  at  $20^\circ C$ . Ceylon oil contains about 10 per cent. of citronellal; sp. gr.  $0.897$  to  $0.912$  at  $15^\circ C$ .; ref. ind.  $1.479$  to  $1.485$  at  $20^\circ C$ .; opt. rot.  $-6^\circ$  to  $-14^\circ$ .

**CITRONELLAL** ( $C_{10}H_{18}O$ )—An aldehyde of the terpene series, found in citronella, lemon-grass, and some varieties of eucalyptus oils; sp. gr.  $0.857$  and b.p.  $208^\circ C$ .

**CITRONELLOL** ( $C_{10}H_{20}O$ ) is described as an unsaturated monohydric alcohol, sp. gr.  $0.857$ , b.p.  $222^\circ C$ ., found in attar of roses, and said to be contained to extent of about 25 per cent. in Spanish geranium oil, also in the *Eucalyptus citriodora* oil; obtainable by reduction from citronellal, and used in perfumery.

**CITRUS FRUITS INDUSTRY**—The composition of some citrus fruit

juices is stated by J. A. Roberts and L. W. Gaddum (*Ind. Eng. Chem.*, **29**, 574 (1937)), as follows :

	pH	Citric Acid, %	Organic Matter, %	Total Sugar, %	Ash, %
Seedling orange ..	3.6	0.74	12.20	9.34	0.45
Blood orange .. ..	3.2	1.11	11.67	8.92	0.48
Valencia orange ..	3.5	0.98	11.39	8.48	0.41
Tangerine .. ..	3.2	1.26	13.93	10.98	0.40
Seedy grapefruit ..	3.0	1.35	9.33	6.20	0.41
Marsh seedless grapefruit	3.0	0.89	6.73	4.78	0.22

The oils of the citrus or Aurantiacæ group include lemon, bergamot, orange, neroli, mandarin, and lime oils, Italy being the largest producer, while the same fruit industry is an important one in California, Spain, France, and the West Indies. Fungal wastage of citrus fruits (and of grapes, oranges, and apples) is effectively controlled by the maintenance of a definite strength of acetaldehyde vapour in the storage vessels, and any of the vapour absorbed by the fruit is destroyed by some mechanism within the fruit.

The waste product (pastaccio) of the citrus fruit industry, that is, the peel and membranes of the pressed fruit, is stated to constitute an excellent binding material for making briquettes when moistened and mixed with coal dust.

See *Citrus Products*, by J. B. S. Braverman (Interscience Publishers, New York).

**CIVET** — An unctuous secretion of revolting odour, from two glands near the anus of the civet cat of Abyssinia (*Viverra civetta*) ; soluble in hot alcohol and ether ; used in perfumery and for scenting soap. When suitably diluted it emits a jasmin-like fragrance.

**CLASSIFICATION, HYDRAULIC** — A term used chiefly in the mining industry to describe methods of size separation (see Elutriation, and Sedimentation).

**CLAYS** — Clays are of secondary origin, being derived from the decomposition and disintegration of various primary rocks, so that they consequently vary in composition and in size of their constituent particles.

Kaolins (terra-alba, China clay, white bole) or various descriptions of white clay are found in large quantities in Cornwall and Devonshire, Ontario, Australia, the U.S.A., British Columbia, the Cape, and elsewhere. Large deposits also occur in the province of Saskatchewan, ranging from the lower grades used for bricks and tiles, to a kaolin which burns quite white. Broadly they may be described as natural hydrated compounds of alumina and silica (aluminosilicic acids) of density 2.5 to 2.7, which become plastic when sufficiently moistened, and in which the proportions of alumina, silica, and water vary greatly. China

clay, as mined in Cornwall and Devonshire on a large scale, conforms nearly to the composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , and is chiefly produced by the disintegration of *pegmatite*—a kind of granite—supposed by some to have been brought about originally in nature by the action of hydrofluoric acid supplemented by that of air and water. Washed down with water and after partial drying pressed into blocks, it is chiefly used in making pottery and stoneware.

The following analyses of residual clays are presented :

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	FeO	CaO	MgO	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$
Scottish boulder clay ..	74.9	12.2	4.3	—	1.6	0.1	1.1	2.6	3.2
Wisconsin .. ..	53.1	21.4	8.5	0.9	1.0	1.4	1.5	0.8	10.8
Virginia .. ..	43.1	25.1	15.2	—	0.6	0.0	1.2	2.5	13.0
Scottish fire-clay ..	52.0	28.0	1.5	—	0.5	—	1.5	—	20.0
London .. ..	51.0	28.0	1.5	—	0.5	—	1.0	—	19.0

Analyses show a considerable range of composition of clays, and also do not furnish sufficient information concerning their properties and values for various applications, although clays of higher content of alumina are generally preferred to those of lower content of alumina for most applications. The outstanding desirable qualities that a clay should possess for industrial uses depend on its plasticity, its behaviour on firing, and ultimately on the product produced by firing.

One method of separating clay from coarse and associated impurities consists in pulverizing it and transferring to a tunnel in which a current of air is used to carry away the finer particles, leaving the coarse ones behind. The tedious process of sedimentation attendant upon treatment by levigation can be hastened by electrical means, the clay being mixed with water and some alkali or other peptizing agent in the nature of an electrolyte, and then subjected to an electric current, by which means the particles of clay, aided by mechanical stirring, are uniformly distributed throughout the suspension, and the impurities (mica, felspar, quartz, and iron compounds) either settle or migrate to the cathode. The purified clay is deposited on the positive pole in a more or less dehydrated state, is much purer than the ordinary product, and, after drying, can be used in making porcelain of high quality.

When heated to  $500^\circ \text{C}$ ., **China clay**, referred to above, is decomposed by the loss of water. In brick-making this water must be liberated *slowly* to avoid harming the product, and so the rate of firing is retarded between  $500^\circ$  and  $700^\circ \text{C}$ . to allow time for this to take place. China clay is used largely as a "filler" in paper-making, in pottery manufacture, in the sizing of textile fabrics, in glass-making, in wall-paper printing, in the manufacture of alum, and to some extent in compounding paints, linoleum, ultramarine, and many other materials.

The following standards have been suggested for china clay : for coating, not more than 0.1 per cent. grit ; for fine papers, not more than 0.5 per cent. ; while low grades, containing from 5 to 10 per cent. mica, should be commercially described as mica clays (J. Strachan). The

higher grades, used in the paper and textiles trades, are designated "bleaching clays," and the potting varieties, such as the "ball clays" of the Bovey basin and Poole district of Dorsetshire, are used for pottery and stoneware, but are distinct from the real kaolins or China clay.

**Colloidal clay** belongs to the class of suspensoids, and is reversible in the sense that the particles can be dispersed in water or thrown out of colloidal solution by suitable electrolytic means. Its quality is improved if minimum viscosity be maintained by the addition of alkali to the clay-casting slip. It is sometimes used for the treatment of dysentery, cholera, and ulcerative colitis; also for the preparation of certain pills and ointments, the clarification of liquids, and in the manufacture of copying-ink pencils, rubber, paints, cleansing powders, toilet articles, etc. It finds use in place of soap in wool-scouring, owing to its capacity of absorbing dirt and grease and removing unsaponifiable matters; but it has the disadvantage of being insoluble, and does not hydrolyse like real soaps. (See "Devolite," and "Stockalite.") "Emol kelect" is a refined preparation of white clay used in making pharmaceutical preparations.

A refractory of the nature of carbonized clay is recommended for use in making filter-beds and high-class acid-resisting ware, having, it is reported, a hardness just short of carborundum.

**Fire-clay**, as used to make fire-bricks, is a natural mixture of kaolin and sand found beneath certain coal-beds, and is almost infusible; it is moulded, dried, and then burned at a high temperature.

The ordinary **common clay** or heavy loam is employed in the making of bricks, tiles, and coarse pottery, and other selected clays are used in the manufacture of Portland and other cements. The presence of iron oxides causes clay to turn red when burned into so-called "ballast."

Several methods of obtaining alumina from clay (of which good grades contain from 30 to 40 per cent.) have been suggested, and it is reported that aluminium sulphate can be readily and economically produced by first of all removing practically all the iron and most of the potash by acid treatment. (See Aluminium Oxide, Bentonite, Cements, Kalsomine, Kaolin, Porcelain, Refractories, Schists, Shale, Sillimanite, and Silica.)

**CLEANSING** — See Washing.

**CLEVES ACID** — See Acid (Cleves).

**CLEVITE** — A mineral hydrated uranium oxide, of crystal system No. 1, and sp. gr. 7.5, containing occluded helium.

**CLOUD CHAMBER** — An instrument making visible the track of a charged particle by fog droplets being formed along the path of the particle. Demonstrated by C. T. R. Wilson, in 1911, to render visible the effect of a single alpha and beta particle.

**CLOVES** — The dried flower buds of *Eugenia aromatica*, an evergreen tree indigenous to the Molucca Islands and cultivated in the Malay Peninsula, Zanzibar, Java, and Ceylon. On distillation in steam, the drug yields from 15 to 20 per cent. of volatile oil which is a pale yellow

liquid, having a pungent odour and containing from 85 to 98 per cent. of eugenol with a small quantity of an inactive hydrocarbon, caryophyllene,  $C_{15}H_{24}$ . Oil of cloves boils at about  $251^{\circ}C$ .; sp. gr. 1.047 to 1.060 at  $15.5^{\circ}C$ .; ref. ind. 1.528 to 1.537 at  $20^{\circ}C$ .; specific rotation  $0.20^{\circ}$  to  $2.30^{\circ}$ . It is soluble in alcohol and ether, possesses strong antiseptic properties, and is used in perfumery, as a flavouring agent, and in medicine. (See Eugenol, and Vanilla.)

**CLUPANODONIC ACID** — See Fish Oils.

**COAGULATION** — The separation of the dispersed phase from the dispersing medium in the case of a colloidal system; egg-albumin is, for example, coagulated by heating or by precipitation with acetic acid. (See "Coagulation," by G. Wiegner (*J.S.C.I.*, **50**, 55 T (1931); Albumins, and Colloid Chemistry.)

**COAL** — **Nature, Distillation, Carbonization, etc.** — Coal is generally regarded as the residual product from the natural decomposition of forests and other vegetable matters during enormous periods of time, and is a very complex mixture of carbon compounds, containing generally some proportion of nitrogen. Deposits of coal are found in all parts of the world. The proved and probable reserves are estimated (1948) to be as follows:—

Country							Millions of Metric Tons
U.S.A.	..	..	..	..	..	..	1,975,000
U.S.S.R.	..	..	..	..	..	..	1,075,000
Germany	..	..	..	..	..	..	289,000
Canada	..	..	..	..	..	..	286,000
China	..	..	..	..	..	..	220,000
United Kingdom	..	..	..	..	..	..	200,000
Poland	..	..	..	..	..	..	138,000
All others	..	..	..	..	..	..	417,000
WORLD TOTAL	..	..	..	..	..	..	4,600,000

"Our National Coal Resources" is the subject of the Second Hinchley Memorial Lecture, by Sir Harold Hartley, appearing in *Trans. Inst. Chem. Eng.*, **13**, 158 (1935).

Coal has been **formed** by the accumulation of vegetable materials, which were later decomposed by bacteria, fungi, and moulds under water. By this process the cellulosic materials underwent progressive decomposition, but the cuticles, seed coats, resins, and waxes proved relatively stable. The succeeding action of pressure and temperature through geological ages converted the residues into coal.

Many solvents have been used in the study of the **nature** of the coal substance, especially (1) pyridine in the work of Wheeler and his colleagues (*Chem. and Ind.*, **50**, 335 (1931)), who conclude that hydrocarbons and resins are requisite for the production of good commercial coke; and (2) benzene under pressure of 500 to 700 atmospheres in the work of Bone and his colleagues (*Chem. and Ind.*, **50**, 407 (1931)), whose conclusion is that no relation is shown between the

hydrocarbon content and the coking power of a coal, but that the coking power is related to a fraction that is insoluble both in absolute alcohol and in a mixture of benzene and light petroleum.

### COAL AND LIGNITE, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country				Millions of Metric Tons	
				Coal	Lignite
Germany .. ..	199				202
United Kingdom ..	233				
France .. ..	47				
Poland .. ..	37				
Belgium .. ..	30				
Czechoslovakia ..	16				15
Netherlands .. ..	14				217
	—			576	
U.S.S.R. .. ..				143	
U.S.A. .. ..				402	
Japan .. ..	40				
British India .. ..	27				
	—			67	
Union of South Africa ..				16	
Sum of above .. ..				1,204	217
WORLD PRODUCTION ..				1,264	273

Coal is an indefinite and variable mixture of some compounds insoluble in pyridine, with cellulosic compounds soluble in pyridine but insoluble in chloroform, and another constituent of resinoid character which can be extracted by certain solvents such as benzene, pyridine, and chloroform, while upon the relative proportions of these bodies the technical value and industrial applications depend.

Bituminous and sub-bituminous coals, when extracted with benzene under pressure, yield from 4.5 to 7 per cent. nitrogenous "humic" bodies, which are mainly responsible for their caking propensities, less than 1 per cent. resin, and important amounts of neutral wax-like nitrogenous substances of low oxygen content.

Aniline used as a solvent is stated to furnish a means of differentiating between grades of coal, the "fat" varieties yielding a relatively higher percentage of soluble matter as compared with the "lean" kinds. The soluble part is richer in hydrogen, poorer in ash, and gives a better coke than the insoluble part.

"Fusain" is a constituent of coal of which a published ultimate analysis is incorporated in the accompanying table. It is said to be a constituent to some extent of all anthracite coals, non-caking, and reduces the coking property of the coal in which it occurs. "Durain" is a granular, hard, homogeneous constituent of coal of dull matt surface; "Vitrain" is a bright coal constituent devoid of preserved plant structure; whilst "Clarain" is a variety possessing a definite, smooth, glossy surface when broken at right angles to the bedding plane. These four banded constituents are found in certain proportions in various coal seams, but while they differ in appearance, they are of approximately similar composition and yield the same products upon being heated. They are to be regarded only as terms to indicate the dull and bright bands of coal and the intermediate materials, and not as indicative of chemical composition, which can only be investigated by study of the action of solvents, of the attack by processes of oxidation, hydrogenation, etc., and of the results of thermal decomposition (pyrolysis).

There are many **varieties** of coal, and they are roughly divided into hard and soft coals, the softer ones being used for fires and gas-making, while the harder ones contain more carbon, give out more heat when burning, and are consequently more useful for steam-raising. Bituminous coal contains from 50 to 80 per cent. of carbon, and anthracite, a hard coal which burns with little smoke or flame, contains from 85 to 95 per cent., but is devoid of bitumen, or nearly so. In burning, coal may be said to give back the heat and light which were originally taken from the sun by the plant-life from which coal is produced, although as domestically used the process is very wasteful and un-scientific.

Average coal contains from 25 to 30 per cent. volatile matter and, when burned or roasted, the products of its destructive decomposition thus effected vary according to its character, the temperature employed, and the proportion of air that gains access to the burning mass. The decomposition of coals begins to yield free carbon at about 500° C., although decomposition proceeds below this temperature.

	No. 2 Llantuit	No. 3 Rhondda	No. 2 Rhondda	Fusain
	Per cent.	Per cent.	Per cent.	Per cent.
Volatile matter ..	37·06	31·50	21·16	—
Fixed carbon .. ..	57·53	66·93	71·20	—
Ash .. .. .	5·41	1·57	7·74	6·33
On dry ash-free coal :				
C .. .. .	82·87	86·70	87·96	78·36
H .. .. .	5·80	5·00	4·35	3·41
O .. .. .	7·76	6·21	4·32	9·97
N .. .. .	1·49	1·45	1·42	1·10
S .. .. .	2·08	0·64	1·95	0·83

**Analyses** of certain coals by S. R. Illingworth are given in the first three columns of table on p. 233, as some illustrations of their composition, which varies greatly, and a comparison is shown with so-called fusain, which is believed to reduce the coking property of coal in which it occurs.

The No. 2 Llantwit coal is used for gas-making, and yields a very porous coke; No. 3 Rhondda coal is carbonized to produce a metallurgical coke, which is dense; and the No. 2 Rhondda coal is a "hard-coking" coal, and also yields a dense coke.

#### ULTIMATE COMPOSITIONS OF SOME BRITISH COALS

(T. J. Drakeley and F. W. Smith)

	Leicester- shire Non- Coking	Derby- shire Non- Coking	Lancashire Cannel		South Wales An- thracite
Carbon (per cent) . .	76.44	78.48	79.55	82.07	88.41
Hydrogen " . .	4.90	5.71	5.81	6.15	3.41
Nitrogen " . .	1.53	0.93	1.19	1.54	1.04
Sulphur " . .	0.83	0.79	0.96	1.48	1.27
Ash " . .	2.52	1.38	5.17	2.38	3.85
Oxygen " . .	13.78	12.71	7.32	6.38	2.02
	100.00	100.00	100.00	100.00	100.00
Radium per gram of ash $\times 10^{12}$ . .	2.66	3.91	1.28	0.042	0.78
Radium per gram of coal $\times 10^{12}$ . .	0.067	0.054	0.066	0.001	0.03

#### SOME CHARACTERISTICS OF TYPICAL U.S.A. COALS

	Penn- sylvania	West Virginia	Kentucky	Illinois
Carbon (per cent.) . .	83	79	81	72
Hydrogen " . .	5	5	5	5
Oxygen " . .	4	5	8	9
Ash " . .	7	8	4	12
Volatile matter (per cent.)	23	33	37	32
Fixed carbon " . .	70	59	60	56
Heating value (B.T.U. per pound) . . . .	14,700	14,200	14,600	12,600
Calories per kilogram . .	8,160	7,870	8,090	7,020

The gross **calorific value** of coal is generally determined by combustion in a Berthelot-Mahler type of bomb calorimeter, and the net value is calculated by deducting the amount of heat in respect of each unit weight of water in the products of combustion.

The plates of inorganic material found in coal seams are derivatives of calcium carbonate, some of the base being replaced by ferrous iron, magnesium, and manganese, and are known as "ankerites."

Among other publications dealing with the constitution and chemistry of coal, see "Action of Solvents on Coal" by R. S. Asbury (benzene extraction) (*Ind. Eng. Chem.*, **26**, 1301 (1934)), (aniline, "Tetralin," and phenol extraction) (*Ind. Eng. Chem.*, **28**, 687 (1936)); G. C. Sprunk and R. Thiessen on "Relation of Microscopic Composition of Coal to Chemical, Coking, and By-Product Properties" (*Ind. Eng. Chem.*, **27**, 446 (1935)); Atkinson *et al.* on "Characteristics of Coal Plasticity" (*Ind. Eng. Chem.*, **29**, 840 (1937)); *The Microscopical Examination of Coal*, by C. A. Seyler (H.M. Stationery Office, London); *Coal. Its Constitution and Uses*, by W. A. Bone and G. W. Himus (Longmans, Green and Co., London); and *The Chemistry of Coal Utilization*, by H. H. Lowry, editor (John Wiley and Sons, New York).

Coal undergoes oxidation by air, one experimental result, which has been published, showing a gain of 3.5 per cent. by weight in one month at 100° C. The alkaline permanganate oxidation of coals yields products of the nature of carboxylic acids of benzene.

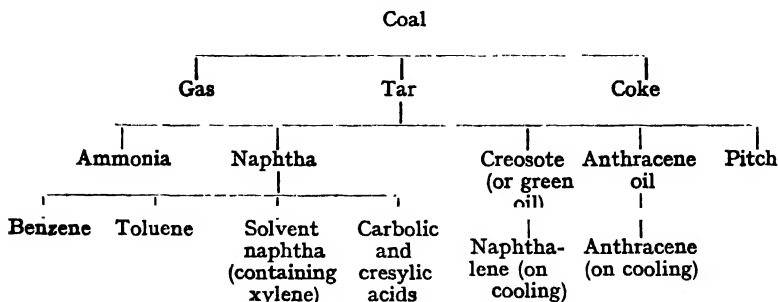
**Spontaneous ignition** or firing of coal is attributed to direct oxidation, and is independent of any contained pyrites; the smaller the coal particles the greater is the danger; it is promoted by moisture, and the greater the oxygen content of the coal, the greater is the liability, so that coal, and particularly pulverized coal, containing more than 10 per cent. oxygen, may be dangerous in storage. It takes but a small proportion of coal dust also to make an explosive mixture, experiments at the United States Bureau of Mines having shown that 0.032 ounce of average Pittsburg coal dust suffices to cause an explosion in contact with flame. The tendency to explode is reported to be proportional to the fineness of division of the dust, and occurs most frequently in fine coal below 1.25 inches, or nut size. When the temperature reaches 140° to 150° F., ignition is likely to occur within a week or so. Storage heaps should be kept as free as possible from excess of air, and external sources of heat should be avoided. Wetting is stated to be without value, but a covering of wet fine coal which keeps away the air is beneficial. Calcium carbonate in precipitated form is used for "stone-dusting" mines, the principal function being to absorb heat, and so prevent a dangerous rise of temperature. The material must be so fine that at least 50 per cent. will pass through a sieve of 200 meshes to the linear inch. (See Mason and Wheeler on "The Inflammation of Coal Dusts: The Effect of the Presence of Firedamp" (H.M. Stationery Office); *Dusts and Dust Explosions*.)

The use of **pulverized** coal by forced air injection is a rival to mechanical stoking for both land and ship boilers. The "Lopulco" installation is a favoured one, the supply of coal and air being controlled

4. Anthracene oil or "yellow oil" (parent of alizarin) at from 280° to 350° C.

5. Pitch left in the retorts ranging up to about 60 per cent. of the total tar.

This may be shown diagrammatically as follows :



By the ordinary method of distillation, tar yields approximately 57 per cent. of oily products and 43 per cent. of pitch, but these proportions vary according to the temperature and pressure used, and it is possible by observing suitable conditions to obtain as much as 73 per cent. oils and only 27 per cent. pitch, the higher percentage of oils being due to some extent to the cracking which takes place when using the "Wilton dehydrating coils," by means of which these results are obtained. (See *Coal, Coke, and Coal Chemicals*, by P. J. Wilson, Jr. and J. H. Wells (McGraw-Hill Book Co., New York).)

**Low-Temperature Carbonization** of coal, brown coal, shale, tar sand, torbanite, peat, wood, and other materials has been the subject of much research work and many processes, but technical and other difficulties must still be overcome to produce thoroughly satisfactory results.

The "Coalite" process employs the coal in a stationary state in narrow cast-iron retorts heated externally. In an account of this process it is alleged that the smokeless fuel so produced is quite satisfactory for household use, has practically the same composition and heat value of the better anthracite coals; further, that each ton of coal yields about 4,000 cubic feet of rich gas, 14 hundredweights of "Coalite," 18 to 20 gallons of crude oil, and from 2½ to 3 gallons of good petrol, while the crude oil can be cracked and thus made to give a further supply of petrol together with fuel oil.

While one object of low carbonization processes is to obtain coke for domestic use free from sulphur and smoke production, another important point to be borne in mind is the possibility of producing petrol and Diesel oils from the liquid products which are rich in aromatic phenols by vapour-phase cracking or hydrogenation. The tar oils are separated as far as can be done under existing circumstances by distillations and extractions with various solvents yielding phenols, from which resins of the bakelite type can be produced, neutral oils (which can be used as liquid fuels and lubricants), waxes, and a number of nitrogenous bases.

Carbonization of washed bituminous coking coal smalls, when conducted in vertical, intermittent, externally heated, narrow diameter (to give internal compression by offering resistance to the swelling action of the plastic charge), cylindrical, cast-iron or alloy-steel pipe retorts, yields 30 to 35 per cent. volatile matter. One long ton of coal thus treated gives (1) 4,000 to 6,000 cubic feet of rich gas (600 to 700 B.Th.U. per cu. ft.), from which about 2 Imperial gallons of crude light oil are scrubbed, (2) about 3 Imperial gallons of crude light oil directly, (3) 17 to 18 Imperial gallons of low-temperature tar, from which about 1 Imperial gallon of light oil is fractionated, and (4) 14 hundredweights (70 per cent. of the coal charged) of graded smokeless fuel ("Coalite"), which has a volatile matter content of 10 to 12 per cent. (See D. Brownlie (*Ind. Eng. Chem.*, 29, 734 (1937)); R. Wigginton, *Coal Carbonization* (Baillière, Tindall and Cox, London); and Coke.)

**Hydrogenation** — When pulverized coal is suspended in a hydrocarbon and treated with hydrogen under pressure of 230 atm. at 430° C. it is largely transformed into liquid hydrocarbons. According to the Report of the Department of Scientific and Industrial Research (H.M. Stationery Office), it is possible to obtain 120 gallons of light spirit accompanied by some heavier oils—that is, about 40 per cent. of the coal—by a process of hydrogenation. Practical difficulties have been experienced by cracking of the iron retorts used and the undue access of air, but the Fuel Research Station has succeeded in constructing an improved fire-clay retort of great promise, and it is reported that by a process of hydrogenation at Billingham, using a semi-commercial plant and clean, dry coal, 60 per cent. by weight has been obtained as refined petrol which has been successfully used in motor vehicles of all descriptions. Calculated on the dry, ash-free coal, the primary yield of liquid products is 75 to 80 per cent. (See Fuel (Liquid).) By way of summary it may be stated that, while some processes of low-temperature carbonization of coal may, under favourable local and economical conditions and particular circumstances affecting the quality of the coal used, be profitably conducted, no one process applicable to coal generally and capable of yielding a satisfactory sulphur-free, smokeless fuel with a sufficiency of petrol and Diesel oil upon a profitable basis has yet been established. Hydrogenation of coal or the products of its low-temperature carbonization is promising.

In the elaborate programme undertaken by the United States Government looking towards increasing the supply of liquid fuels, the hydrogenation of coal is one of the projects assigned to the U.S. Bureau of Mines. Treatment of carboniferous shale is another of the projects, and still another is the use of natural gas. (See Fuel (Liquid) for Fischer-Tropsch process.)

**Tars** — The following information respecting coke and gas tars is taken from a work on coal tars by G. Malatesta (E. and F. N. Spon, London):

Coke-furnace tar is distinguished from that of illuminating gas production by a lower amount of free carbon and the different amounts of the various contents. The free carbon of coke-furnace tar does not

exceed, as a rule, 10 to 12 per cent., and frequently the content is between 2 and 6 per cent. As the carbon varies, so do the other constituents of tar. The distillation of different coke tars has given the following results :

	1	2	3	4	5	6	7	8
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Water .. ..	2.0	2.69	2.3	Trace	6.60	3.20	3.40	3.70
Light oil .. ..	1.5	1.38	3.7	6.5	2.30	0.80	4.10	3.20
Middle oil .. ..	7.0	3.46	9.8	10.5	10.20	5.00	10.70	10.50
Heavy oil .. ..	14.0	9.93	12.0	7.6	8.00	8.40	8.60	7.40
Anthracene oil ..	14.0	24.76	4.3	44.3	26.70	22.70	19.00	16.80
Pitch .. ..	60.0	56.44	67.0	30.5	49.19	58.60	55.40	57.20
Loss .. ..	1.5	1.34	0.9	0.4	0.28	1.30	1.60	0.20
Specific gravity ..	1.16	1.145-1.191	1.17	1.1198	—	—	—	—

According to Schniewind, the variations in composition of gas tars and coke-furnace tars obtained from various foreign coals are given by the table below.

**Coal Cleaning** — A process for the utilization of colliery waste consists in grinding it to powder, mixing with three or four times its weight of water, and then agitating the mixture after addition of a small proportion of an oil or tar distillate. This produces a froth, in which the particles of coal adhere to the air bubbles, forming a scum of purified coal which can be skimmed off and dried, whilst the heavier associated impurities (shales and "brasses") settle. One pound of the added reagent is stated to suffice for each ton of the coal mixture, and the coal thus obtained is stated to be excellent for coking and making briquettes.

By the so-called "Trent" process of separating mineral matter from coal (available also for utilizing poor quality coals and lignites, which would not otherwise be economically used) an oil reagent is employed, resulting in the production of an admixture of coal with heavy petroleum

Fractions	Coke-furnace Tar		Gas Tar		
	Canadian Coal	Westphalian Coal	German Coal	American Coal	
				Good	Bad
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Light oil .. ..	1.26	6.55	2.5	1.65	6.14
Middle oil .. ..	14.73	10.54	2.5	10.66	5.03
Heavy oil .. ..	7.07	7.62	25.0	8.18	7.50
Anthracene oil ..	21.38	30.55	10.0	14.05	11.71
Pitch .. ..	53.03	44.35	60.0	61.16	68.25
Water .. ..	1.52	Trace	—	1.81	—
Loss .. ..	1.01	0.39	—	2.41	1.37
Free carbon .. ..	8.10	—	25.00	—	48.4
Specific gravity ..	1.088	1.1198	1.155	—	1.255

oil, which is said to yield a plastic fuel. A non-caking coke is produced upon distillation, and the total heating value of the gas from 1 ton of such "amalgam" (consisting of about 70 per cent. coal and 30 per cent. oil) proved, in one experiment, to be 6,109,000 B.Th.U., as against 2,460,000 units for the combined gases from coal and oil, and the total quantity of gas was greatly increased at the expense of the tar. The experiment in question was conducted at 600°C. in an electrically heated apparatus.

R. Lessing's method of coal cleaning is one by which clean coal can be produced at a cost comparing favourably with washing processes, the product being low in ash and giving a reduced cost for the production of pig iron. This "gravity separation" method removes first as much as possible of the dust, after which the "float and sink" application follows, calcium chloride solution of sp. gr. 1.4 or fine suspensions of clay of the required density being used. (See *The Cleaning of Coal*, by Chapman and Mott (Chapman and Hall, London); and *The Efficient Use of Fuel*, p. 20 (H.M. Stationery Office, London).)

See Berginization, Brown Coals, Coal Ash, Coke, Coke-Ovens, Colloidal Fuel, Gas (Coal), Hydrogen (Hydrogenation), Lignite, Ores, Peat, and Tar.

**COALESCENCE** — See Emulsions.

**"COALITE"** — See Coal.

**COAL ASH** — Over 95 per cent. of the mineral matter that can be separated from coal consists of clay, limestone, and pyrite, and over 95 per cent. of the ash of burned coal is made up of four oxides, namely, silicon oxide, aluminum oxide, calcium oxide, and ferric oxide, when calculated on a sulphate-free basis.

Coal ash has been examined for the rarer elements and certain horizons of Northumbrian coal have yielded an ash containing notable quantities of the oxides of gallium and germanium.

The ash-softening temperature which is an important consideration in the formation of clinker in the fire-box of a furnace, is a function of the relative proportions of the four oxides mentioned. An excellent contribution to the study of these relations is given by G. Thiessen, C. G. Ball, and P. E. Grotts, *Ind. Eng. Chem.*, **28**, 355 (1936) as shown in the accompanying table.

Softening Temperature of Ash, °F.	COMPOSITION OF COAL ASH			
	SiO <sub>2</sub> Per Cent.	Al <sub>2</sub> O <sub>3</sub> Per Cent.	CaO Per Cent.	Fe <sub>2</sub> O <sub>3</sub> Per Cent.
1,990	31.1	16.3	2.8	47.7
1,990	41.2	13.1	15.8	14.9
2,320	58.5	23.9	4.1	13.4
2,380	50.8	28.2	2.7	13.8
2,520	54.9	26.3	0.5	12.0
2,520	56.0	31.8	2.4	9.8
2,800	53.5	30.4	0.9	9.4

**COAL GAS** — See Gas.

**COAL HYDROGENATION** — See Berginization, and Coal.

**COAL TAR** — See Coal, and Tar.

**COBALT (Co) and its Compounds** — Atomic weight, 58·94. See Elements for other data. Cobalt occurs in nature in several combinations with arsenic and sulphur, including *smaltine* (*smaltite*), or *speiss cobalt* (cobalt arsenide,  $\text{CoAs}_2$ ) of crystal system No. 1, and sp. gr. 6·5–7·2; *cobalt glance* (*cobalite*) (cobalt sulpharsenide,  $\text{CoAsS}$ ), a compound mineral sulphide and arsenide ( $\text{CoS}_2 + \text{CoAs}$ ), of crystal system No. 1, and sp. gr. 6·0; and *cobalt bloom* or *erythrite* (a hydrated arsenate of cobalt,  $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ , of crystal system No. 5, and sp. gr. 2·95. The chief sources are Canada, and Queensland, Australia.

The metallurgical treatment of certain cobalt ores consists of a combination of dry and wet processes designed to separate associated nickel by precipitation of cobalt sesquioxide ( $\text{Co}_2\text{O}_3$ ) with bleaching-powder solution, the other cobalt compounds being prepared from the purified product, and the metal obtained therefrom by reduction processes, as, for example, with carbon in the electric furnace, or by means of hydrogen, or by the "thermit process," using aluminium powder. The crude cobalt oxide prepared as described contains some nickel, and although most of it can be removed by treatment with hydrochloric acid, it still contains a small proportion. To obtain analytically pure cobalt

#### COBALT ORE, WORLD PRODUCTION

Annual average for the three-year period 1937–1939

Data arranged and rounded off by the Editor.

	Country				Cobalt Ore as Co Content Metric Tons
Canada	..	..	..	..	260
Burma	..	..	..	..	260
Northern Rhodesia	..	..	..	..	1,970
Belgian Congo	..	..	..	..	1,500
French Morocco	..	..	..	..	600
					<hr/> 4,070
Sum of above	..	..	..	..	<hr/> 4,590

Cobalt ore is also produced in Bolivia, Chile, China, Finland, Germany, Italy, Japan, Mexico.

oxide, G. T. Morgan and Main Smith have devised a process as follows: the ore is first of all freed from associated arsenic in part, and the calcined speiss (consisting largely of arsenides and oxides) is dissolved in hot concentrated hydrochloric acid; the iron and arsenic are

removed as ferric arsenate by hot milk of lime ; the metals of the second group as sulphides by hydrogen sulphide, and the remaining iron as ferric hydroxide by milk of lime. From the final liquid the oxides of cobalt and nickel are fractionally precipitated with bleach liquor, the cobalt being separated nearly quantitatively before nickel. From the crude cobalt oxide purpureo-cobalt chloride ( $\text{CoCl}_2 \cdot 5\text{NH}_3$ ) $\cdot \text{Cl}_2$  can be readily obtained, and from this compound analytically pure cobalt oxide.

Cobalt-tungsten-chromium alloys constitute good abrasives and can be deposited on certain iron and steel surfaces to protect them from wear, and also used for repairing the worn surfaces ; while cobalt-tungsten-carbide alloys are successfully employed in machining metals at high speeds and increasing the life of cutting tools. The hardness of these alloys on the Brinell scale varies from 1,250 to 1,400 as compared with 1,000 for the hardest steel.

Presence of the element cobalt in minute traces has been shown (1936) to be essential in preventing certain types of anæmia both in children and in cattle.

Metallic cobalt is pinkish-white, very hard, ductile, tenacious, and strongly magnetic. It is used in making many alloys, particularly cobalt steels for permanent magnets in radar and signalling equipment, and for resistance to high temperatures such as those encountered in jet engines, cobalt-chromium high-speed steel tools for cutting purposes, and in the field of electroplating. (See H. E. Kershaw on "Cobalt-Chrome Magnet Steels" (*Ind. Chem.*, **5**, 47 (1929)) ; *Cobalt* by Roland S. Young (Reinhold Publishing Corp., New York) ; and *Stellite*.)

There are three **oxides**, namely,  $\text{CoO}$ ,  $\text{Co}_2\text{O}_3$ , and  $\text{Co}_3\text{O}_4$ , all of which can be used as pigments, the monoxide being soluble in acids forming the ordinary cobaltous salts, including the soluble pink-coloured chloride, nitrate, and sulphate. All cobalt compounds give a deep blue colour to glass or to a bead of borax when melted together. (See Boron (Borax).)

**Smalt (Silicate of Potash and Cobalt)** is a fine blue glass used for colouring enamels, otherwise as a pigment and in the ceramic industries. It is prepared by roasting smaltine with quartz sand and potash, the fused mass being subsequently ground to a fine degree beneath water. Its superiority over ultramarine as a pigment lies in the fact that it is a fast colour under practically all conditions, but for many purposes it has been superseded by manufactured ultramarine.

**Cobaltous Chloride** ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), a salt soluble in water, finds use as a colouring material, and when gently heated to  $120^\circ \text{C}$ . loses its pink colour and becomes blue by the loss of its water of crystallization ; hence its employment in preparing sympathetic inks, the faintly written pink words becoming visibly blue upon warming of the paper on which they are written.

**Cobaltous Nitrate** ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) is a reddish-brown, crystalline salt, soluble in water, also used in preparing sympathetic inks.

**Cobaltous Sulphate** ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ) is a pink, crystalline salt, soluble in water, and used in ceramics, whilst combinations known as

cobaltous oleate, linoleate, and resinate are employed as varnish driers. The **oleate** is made from cobaltous chloride and sodium oleate, and the **resinate** by heating a mixture of a cobalt salt with rosin oil.

**Cobaltous Acetate** ( $\text{Co}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ ) is a reddish, crystalline salt of deliquescent nature, soluble in water; used in the preparation of sympathetic inks and as a drier in respect of linseed oil.

**Cobaltous Arsenate** ( $\text{Co}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) is a violet powder, insoluble in water, used, as is also the natural erythrite, for painting on glass and porcelain.

**Cobaltous Carbonate** ( $\text{CoCO}_3$ ) — A rose-coloured insoluble powder used as a pigment.

**Cobaltous Phosphate** ( $\text{Co}_3(\text{PO}_4)_2 \cdot 2\text{H}_2\text{O}$ ) — An insoluble pink powder used as a pigment and for painting porcelain.

**Cobaltous Tungstate** ( $\text{CoWO}_4$ ) — An orange-coloured insoluble powder used as a pigment.

**Cobalt Carbonyl** — At 50 to 100 atmospheres' pressure and at about  $250^\circ \text{C}$ . cobalt unites with carbon monoxide, forming shellac-coloured crystals of the chemical proportions  $\text{Co}(\text{CO})_4$ , but of double this molecular weight, and if this be heated to  $60^\circ \text{C}$ . it quickly loses one-fourth of its CO, forming the tri-carbonyl  $\text{Co}(\text{CO})_3$ .

**Cobaltamines (Ammonia-Cobalt Compounds)** — A great number of both cobaltous and cobaltic compounds of this class are known, usually exhibiting the characteristic co-ordination number of six. The tetrammine series, flavo- and praseo-cobalt chlorides have the composition  $(\text{CoCl}_2 \cdot 4\text{NH}_3)\text{Cl}_2$ , hexammino cobaltic chloride is  $(\text{Co} \cdot 6\text{NH}_3)\text{Cl}_3$ , the luteo series. Purpureo-cobalt chloride is chloro-pentammine-cobaltic chloride  $(\text{CoCl} \cdot 5\text{NH}_3)\text{Cl}_2$ . (See Ammines.)

Many of the cobalt salts, including the hydroxide, resinate, borate, are used as driers in the manufacture of paints and varnishes. The quantity of cobalt compounds used in the pottery and enamel trades is relatively small, as the amount required for blue colouring, decorative designs, and neutralizing the yellow tinge in earthenware is generally about only  $\frac{1}{8000}$  part.

**COBALT BLUE (Thénard's Blue)** — Cobalt aluminate obtained by heating together cobalt sulphate and alum, phosphoric acid and zinc oxide being sometimes incorporated to vary the tints.

**COBALTIME (Cobaltite)** — See Cobalt.

**COCA** — The dried leaves of plants of the genus *Erythroxylaceæ*. Bolivian coca is obtained from *Erythroxylum coca*, which grows abundantly on the slopes of the Andes and is cultivated in Bolivia, and Peruvian or Truxillo coca is derived from *Erythroxylum truxillense*, a shrub indigenous to Peru and cultivated in Java. Coca contains from about 0.5 to 1.5 per cent. of total alkaloids comprising cocaine, cinnamyl-cocaine and  $\alpha$ - and  $\beta$ -truxillines. The drug also constitutes a source of ecgonine from which cocaine may be synthesized. (See Waxes (Coca).)

**COCAINE** ( $C_{17}H_{21}O_4N$ ) — A colourless, crystalline alkaloid, namely, methylbenzoyllecgonine, of m.p.  $98^{\circ}C$ . It may be obtained from coca leaves by admixture with lime and subsequent extraction with solvent naphtha; cocaine is obtained from the crude mixture of alkaloids by purification or by acid hydrolysis and subsequent methylation and benzylation of the ecgonine thus prepared. It is soluble in alcohol and ether; insoluble in water. Cocaine is used in medicine as a local anæsthetic, particularly in the form of its hydrochloride which is soluble in water. (See Anæsthetics, Coca, and Procaine.)

**COCARBOXYLASE** — Enzyme present in animal tissues and yeast. It can be hydrolysed with dilute acids to yield the phosphoric ester of vitamin B, and free phosphoric acid. It is important in the metabolic processes of animals. (See Enzymes.)

**COCULUS INDICUS (Levant Berries)** — The dried, ripe fruit of *Anamirta paniculata*, a climbing shrub growing on the coasts of Malabar and Ceylon. The seeds contain from 1 to 1.5 per cent. of picrotoxin ( $C_{30}H_{34}O_{13}$ ), a bitter principle which is a powerful convulsive poison and is used in medicine as a stimulant in the treatment of morphine and other types of narcotic poisoning. The roasted berries are sometimes used for poisoning fish. (See Picrotoxin.)

**COCHINEAL (Coccus Cacti)** — The dried female insects of *Dactylopius coccus* containing the eggs and larvæ, which live on the branches of various plants (*Nopalea*) indigenous to Mexico but also cultivated in Guatemala, the West Indies, Teneriffe, Madeira, Algeria, and Java. The female insects only are collected, killed by exposure to the fumes of burning sulphur, and dried in the sun. In the dried state, cochineal is an odourless, dark red, granular material, which is readily reduced to a deep red powder. Boiled with water, it yields a dark red liquid, which can be changed to other colours by the addition of various chemicals. It is used as a colouring agent in foods and medicines, and also in the preparation of carmine and carmine "lakes" and for the dyeing of wool and silk.

The colouring matter may be prepared by treating the aqueous extract of cochineal with potassium acid tartrate, alum or potassium acid oxalate to coagulate the proteins, and the colouring matter is carried down with the precipitate. It is soluble in water, alcohol, and ether and contains about 50 per cent. of carminic acid ( $C_{22}H_{22}O_{13}$ ), which gives well defined salts. (See Kermes.)

Wild cochineal, obtained from *Dactylopius tomantosus*, is used for retarding the growth of the prickly pear in areas affected by the growth of that plant. The insect destroys the plant by sucking away the juice. (See Waxes (Coccerin).)

**COCKLE-BURR OIL** — A seed drying-oil, obtained by cold pressure (about 30 per cent.) from the kernels of *Xanthium echinatum*. It is a light, sparkling oil of pleasant odour and nutty flavour, with a sp. gr. of 0.9251 at  $15^{\circ}C$ , i.v. (Hanus) 140.8, and sap. v. 190.2.

**COCOA** — See Cacao.

**COCOA-BUTTER** — See Cacao.

**COCONUT OIL** (*Cocoa-Nut Oil*) — The semi-solid, white, edible fat, extracted by pressure from the kernels of the coconut, the fruit of *Cocos nucifera*. The fully matured nuts fall when ripe and each yields on average about 8 oz. of dried kernels (copra) which contains from 30 to more than 40 per cent. of the fat. Coconut oil is soluble in alcohol, ether, and carbon disulphide, has a sp. gr. of about 0.925; ref. ind., 1.4485 to 1.4495 at 40° C.; sap. v., 255 to 258; i.v., 7 to 10; Reichert-Meissel value, 7.15 to 7.54; m.p., 26° to 28° C.; solidifying point, 22° to 23.5° C. It has been shown that the oil from the testa of the coconut differs from that of the kernel in iodine value, and saponification value, that from the parings having higher values.

Supplies come from the Malabar coast, India, Ceylon, South Sea Islands, Kenya Colony, Tanganyika, Uganda, Northern Rhodesia, Nyasaland, British Guiana, Malaya, Jamaica, and Philippine Islands. Commercial grades are known as "Cochin," "Ceylon," and "Copra Oil." Coconut oil is used in the manufacture of soap, candles, confectionery, margarine; and for cooking.

According to E. F. Armstrong and others, the fatty acids of the kernel oil (contained as glycerides) include octoic (2 per cent.), lauric (28 per cent.), myristic (22 per cent.), palmitic (12 per cent.), oleic (23 per cent.), linoleic (10 per cent.), and possibly 1 per cent. of stearic acid. The oil obtained from the parings of the testa contains octoic (9 per cent.), decoic (4.5 per cent.), lauric (51 per cent.), myristic (18.5 per cent.), palmitic (7.5 per cent.), oleic (5 per cent.), linoleic (1 per cent.), and possibly stearic acid about 3 per cent.

The residual cake contains from 5 to 10 per cent. of oil, and is used as a cattle food, whilst the fibrous portion of the nut provides the coir used for matting, cordage, etc. A spirituous drink known as coconut toddy is prepared from the sap drawn from the unopened flower spathe of the same palm and its characteristics are described by Cowap and Geake, *Analyst*, 57, 627 (1932). (See Copra.)

**CODEINE** (*Morphine Methyl Ether*) ( $C_{18}H_{21}O_3N, H_2O$ ) — A colourless, crystalline alkaloid of m.p. 155° to 156° C.; soluble in water (1 in 120), and in alcohol (90 per cent.) (1 in 2). Codeine is obtained from opium or by methylation of morphine. Used in medicine as a mild hypnotic and sedative in cough mixtures. (See Opium.)

**COD-LIVER OIL** — See Fish Oils.

**COFFEE** — The beans consist of the roasted, decorticated seeds of *Coffea arabica* (N.O. Rubiaceæ), a native of Southern Abyssinia and cultivated in Brazil (60 per cent. of the world's production), Colombia (11 per cent.), Salvador, Guatemala and Mexico (8 per cent.), and East Indies (5 per cent.). The berries, after collection may be sun-dried and passed between rollers to separate the beans from their outer coats or, alternatively, the fresh berries are run through a pulper to remove the greater part of the fleshy tissues and the remainder of the pulp is removed from the endocarp by fermentation and washing. The beans are then dried in the sun or by artificial means

and are finally passed through shelling and polishing machines. After import, the beans are roasted to develop the aroma. Raw coffee contains caffeine (theine) ( $C_8H_{10}O_2N_4$ ), fixed oil, protein, carbohydrate, and caffetannic acid (chlorogenic and coffalic acids). Roasting reduces the caffetannic acid content and caramelizes a part of the carbohydrate. Of roasted natural coffees, those from Novo Redondo have been shown to contain the highest proportion of caffeine (2.43 per cent.), whilst those from Mozambique contain the least (0.72 per cent.). The solid fatty acid constituents of coffee-berry oil have been determined as 29 per cent. palmitic, 3 per cent. daturic, 14 per cent. carnaubic, 2 per cent. oleic, and 50 per cent. linolenic acids.

Substitutes used as adulterants for coffee include chicory, caramel, roasted cereals, dandelion-root, and figs. Coffee parchment (endocarp) is sometimes used as an adulterant of bran and sharps. Several processes have been patented for the production of caffeine-free coffee; one such process depends upon extraction with water, removal of the caffeine from the aqueous extract, and the return of the residue to the coffee. (See *Structure and Composition of Foods*, by A. L. and K. Winton, Vol. IV (John Wiley and Sons, New York); L. W. Elder, Jr., *Ind. Eng. Chem.*, **29**, 267 (1937); and Caffeine.)

**COGNAC OIL** — See Cēnanthic Ether.

**COHUNE OIL** — Extracted from the kernels of the cohune palm (*Attalea cohune*), which yields on average 68 per cent., and grows in British Honduras, Guatemala, and Mexico. It is a yellowish, semi-liquid fat, of m.p.  $18^{\circ}$  to  $20^{\circ}$  C., sp. gr. 0.868, sap. v. 252, and i.v. 11 to 13.7. It is soluble in ether and benzol, is used in candle and soap making, also for cooking purposes; resembles coconut oil, and can be used in place of it for many purposes.

**COINAGE** — See Copper, Gold, Nickel, and Silver.

**COIR** — The outer coating or fibres of the coconut, used for making matting, brushes, small cables and rigging, and as a spinning material.

**COKE** — Certain varieties of coal (see Coal) yield excellent coke when subjected to high temperature in the absence of air (carbonization or pyrolysis). Hard and coherent cokes are required in the iron blast-furnaces, and for other metallurgical purposes. Lower grades of coke may be utilized for domestic heating. Since volatile matter is absent, due to the process of formation, coke is a smokeless fuel. Coke is an ideal solid fuel for house use, and burns completely in one stage with brilliancy and power.

The "shatter test" for coke, a test of great importance for metallurgical coke as an indication of the burden of charge it can carry, consists in dropping 50 lbs. weight of it on to an iron plate, the "shatter index" being the percentage of the broken material remaining upon a 2-in. sieve. This index and the combustibility of coke are stated to be intimately related to the sp. gr., porosity, and water-absorbing capacity of the material (H. V. A. Briscoe). The standard method for the shatter test as adopted by the Midland, Northern and Scottish Coke Research Committee is described in *Chem. and Ind.*, **49**, 320 (1930).

See *Coke and its Uses*, by E. W. L. Nicol (E. Benn, Ltd., London); *Coke-Oven Managers' Association Year Book* (Benn Bros., London); *Coke for Blast Furnaces*, by Mott and Wheeler (Colliery Guardian Co., London); Coal, and Coke-Ovens.

### COKE PRODUCTION BY COUNTRIES FOR THE YEAR 1944

Authority: *The Mineral Industry of the British Empire and Foreign Countries* (Imperial Institute)

Data arranged and rounded off by the Editor.

Country	Coke Ovens Coke Long Tons	Gas Works Coke Long Tons	Total Coke Long Tons
United States.. ..	56,400,000	3,500,000	—
Germany .. ..	51,600,000	—	—
Great Britain .. ..	14,100,000	11,500,000	—
U.S.S.R. (Russia) ..	—	—	16,400,000 (1939)
Japan .. ..	—	—	3,700,000
Canada .. ..	3,100,000	200,000	—
France.. ..	2,900,000	300,000	—
Poland .. ..	3,200,000 (1943)	—	—
Australia .. ..	1,500,000	1,000,000	—
Belgium .. ..	2,000,000	—	—
Netherlands .. ..	1,600,000	400,000	—
India .. ..	—	—	2,000,000
Italy .. ..	1,600,000 (1942)	—	—
Spain .. ..	800,000	200,000	—
Sweden .. ..	—	—	600,000

### COKE PRODUCTION IN THE UNITED STATES OF AMERICA SINCE 1896

Quantities in millions (10<sup>6</sup>) of short tons (2,000 pounds).

Year	Beehive Coke	By-product Coke	Gas Retort Coke	Petroleum Coke	Total
1896	12.0	0.1	—	—	12.1
1900	19.5	1.1	1.5	—	22.1
1907	35.1	5.5	1.7	—	42.3
1912	32.9	11.1	2.4	—	46.4
1916	35.5	19.1	2.9	0.3	57.8
1920	20.5	30.8	3.2	0.6	55.1
1923	19.4	37.6	2.8	0.7	60.5
1929	6.5	53.4	2.8	1.9	64.6
1937	3.2	49.2	2.0	1.3	55.7
1945	5.2	62.1	0.9	2.0	70.2

Metallurgical coke is produced in coke-ovens of various types, specially selected coal being used for this high-temperature process, yielding tar (about 3 per cent. of the coal carbonized), 1 per cent. ammonium sulphate, and crude benzol (2 gallons per ton of coal carbonized). Coke-oven gas is rich in hydrogen content, a typical analysis being 53 volume per cent. of hydrogen, 35 of methane, 3 of carbon monoxide, and 2 of ethylene. (See J. E. Foxwell, on "By-Product Coking Industry" (*Chem. and Ind.*, **52**, 49 (1933)); *Coke-Oven and By-Product Works Chemistry*, by T. B. Smith (C. Griffin and Co., Ltd., London); Coal, and Nitrogen.)

**COLA NUTS** — See Kola Nuts.

**COLCHICINE** ( $C_{22}H_{25}O_6N$ ) — A yellow, crystalline alkaloid extracted from the seeds and corm of *Colchicum autumnale*; melting point when dry, about 145° C.; soluble in water (1 in 22) and in alcohol, chloroform, and ether. It has a bitter taste and is used in medicine as a remedy for gout. (See Colchicum.)

**COLCHICUM** — The meadow saffron, *Colchicum autumnale*, a genus of Liliaceæ, grows wild in many parts of England and throughout Europe. The dried corm contains about 0.4 per cent. of colchicine together with starch, gum sugar and fat. The dried ripe seeds contain from 0.3 to 0.6 per cent. of colchicine and an oil of sp. gr. 0.9176 sap. v. 184.3 and i.v. 128.5. (See Colchicine.)

**COLCOTHAR** — A crude red oxide of iron obtained by roasting green copperas (ferrous sulphate). (See Iron (Ferric Oxide).)

**COLEMANITE (Borate Spar)** — See Boron, and Pandermite.

**COLEY'S ZINC PROCESS** — See Zinc.

**COLLAGEN** — See Tanning.

"**COLISTATIN**" — See Succinylsulphathiazole.

**COLLODION** — A solution of cellulose tetranitrate, or nitrated cellulose in ether and alcohol largely used in photography, also as a coating for various materials, in making patent leather, and in medicine.

Flexible collodion is used as a protective application for cuts and abrasions, and contains 2 per cent. pyroxylin with colophony and castor oil in alcohol and ether.

**COLLODION COTTON** — A product of the nitration of cellulose prepared in much the same way as nitrocellulose, containing about 12 per cent. nitrogen, and used in the manufacture of silk substitutes and lacquers.

**COLLOIDAL STATE** — When coarse sand is shaken with water it quickly settles when the shaking stops. The finer the sand the more slowly it settles. If the sand is powdered finely enough and stirred into water it will not settle at all but remain dispersed in the water. These particles of sand which do not settle out on standing are larger than molecules and are said to be in the **colloidal state**. They cannot be seen with the unaided eye or even with a good microscope, they are not removed with the best filter papers, they show the Tyndall beam

(Tyndall effect) when light is passed through the solution, they show the characteristic Brownian movement when viewed with an ultramicroscope. When the diameters of these particles are measured they are found to vary in the range of  $1\text{m}\mu$  to  $100\text{m}\mu$  ( $1\text{m}\mu=10^{-7}$  cm.). It is to be noted that the term colloid, meaning glue-like, now has no significance, for most, if not all, substances can be prepared in the "colloidal state."

The colloidal state is determined almost entirely by particle size, the limits of which are about  $1\text{m}\mu$  to  $100\text{m}\mu$  in diameter. Particles whose diameters are smaller than  $1\text{m}\mu$  are in the realm of the molecular state and form true solutions that do not show the Tyndall beam, nor can they be seen in the ultramicroscope. Particles larger than  $10,000\text{m}\mu$  are known as coarse dispersions (if in suspension) or precipitates and can be seen with the naked eye or in the ordinary microscope. An emulsion (see Emulsions) contains droplets that vary in diameter from  $100\text{m}\mu$  to  $10,000\text{m}\mu$ . In the first table the spectrum of particle size is shown.

The two phases of a dispersed system, involved in the colloidal state, are the **dispersed state** (the phase forming the particles) and the **dispersion medium** (the phase in which the particles are distributed). Since either phase may be liquid, gaseous, or solid, there are a number of possible types of dispersed systems. For example, smoke and dust are solids dispersed in a gaseous medium; clouds, fogs, and mists consist of liquids dispersed in air (F. T. Gucker, Jr., "Aerosols," in *Scientific Monthly*, 48, No. 6 (June, 1949)); ruby glass consists of colloidal particles of gold dispersed in a glass-like medium; and a foam consists of air dispersed in a liquid.

Colloidal systems having a liquid phase for the dispersing medium are divided into **lyophilic sols** (solvent loving) and **lyophobic sols** (solvent hating). The essential differences between the two groups are:

#### *Lyophilic sols*

1. Particles are difficult to detect in the ultramicroscope.
2. Particles may migrate in either direction or not at all under an electric potential.
3. Small quantities of electrolytes have little effect.
4. Viscosity is greater than the medium.
5. Surface tension is often lower than that of the medium.

#### *Lyophobic sols*

1. Particles are easily detected in the ultramicroscope.
2. Particles migrate under electric potential.
3. Small quantities of electrolytes cause precipitation.
4. Viscosity is about the same as the medium.
5. Surface tension is about the same as the medium.

Examples of lyophobic colloids include metals, sulphur, sulphides and insoluble salts while gums, starches, proteins, and soaps are lyophilic colloids.

When a substance is dispersed into the colloidal state new properties manifest themselves. The pull of gravity is somewhat counteracted,

SPECTRUM OF PARTICLE SIZE AND APPROXIMATE RANGE OF SOME CHARACTERISTIC PHENOMENA

Scale Units	$10^0$	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$	$10^{-5}$	$10^{-6}$	$10^{-7}$
mm								
$\mu$	$10^3$	$10^2$	$10^1$	$10^0$	$10^{-1}$	$10^{-2}$	$10^{-3}$	$10^{-4}$
m $\mu$	$10^6$	$10^5$	$10^4$	$10^3$	$10^2$	$10^1$	$10^0$	$10^{-1}$
Precipitates and Coarse Emulsions				Emulsions		Colloidal State		Molecular State

while surface tension, electric charge, and other forms of energy are greatly increased. Gold, having a specific gravity of 19.3 and a yellow colour, upon being colloiddally dispersed in water forms a hydrophobic (water hating) colloidal system having a blue colour, or if very finely dispersed a red colour.

The adsorption ability of the colloidal state (see Adsorption) is due to the huge surface area of the dispersed substance. If a cubic particle of a substance 1 cm. on an edge is dispersed to the colloidal state having a diameter of  $1\text{m}\mu$  ( $10^{-7}$  cm.) there will be  $10^{21}$  particles having a total area of 6,000 square metres or  $1\frac{1}{2}$  acres. Since adsorption is a surface phenomenon the initial particle having 6 sq. cm. of area could only have a limited capacity for adsorption when compared to the area available when the particle is dispersed to the colloidal state. (See second table.)

Colloidal gold-in-water systems have been kept for years with no sign of the gold settling out although it is 19.3 times as dense as water. Why doesn't the gold settle out? Why do colloidal particles remain in suspension? There are at least three good reasons for the stability of the colloidal state.

(1) The molecules of the dispersion medium by their kinetic motion continually bombard the large colloidal particles, giving to them the characteristic random Brownian movement which has a tendency to prevent settling of the dispersed phase. (See Brownian Movement, and Tyndall Effect.)

THE INCREASE IN TOTAL SURFACE AREA OF ALL PARTICLES UPON DIVIDING EACH SIDE OF A CUBE ( $1\text{ cm.}^3$ ) SUCCESSIVELY INTO TEN EQUAL PARTS

Number of Cubes	Length of Edge cm.	Total Surface Area sq. cm.
1	1	6
$10^3$	$10^{-1}$	$6 \times 10$
$10^6$	$10^{-2}$	$6 \times 10^2$
$10^9$	$10^{-3}$	$6 \times 10^3$
$10^{12}$	$10^{-4}$	$6 \times 10^4$
$10^{15}$	$10^{-5}$	$6 \times 10^5$
$10^{18}$	$10^{-6}$	$6 \times 10^6$
$10^{21}$	$10^{-7}$	$6 \times 10^7$
$10^{24}$	$10^{-8}$	$6 \times 10^8$

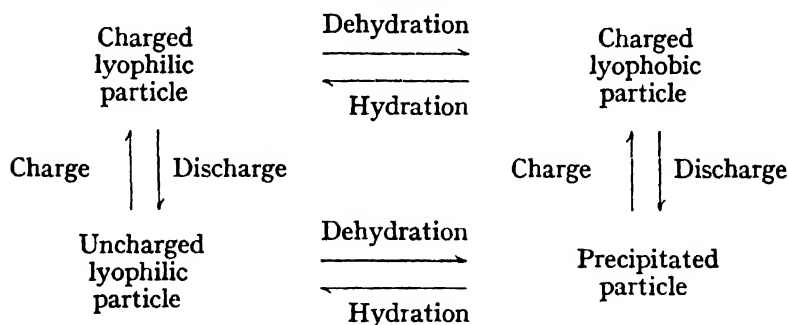
(2) Dispersed colloidal particles, especially the lyophobic particles, when placed in an electrolytic cell migrate towards one of the electrodes, showing that the particles are charged. For a given substance all the colloiddally dispersed particles have the *same* type of charge. Thus, if the particles tend to settle they will come close to other particles having the same charge and will be repelled by electrostatic forces (like charges

repel, unlike charges attract). The type of charge that a substance will take when dispersed colloiddally is generally specific for each material. Thus ferric hydroxide takes a positive charge, while arsenious sulphide takes a negative charge.

(3) A protective film of a gelatine-like substance about each particle will prevent coagulation and thus help stabilize the dispersed particle. The accompanying diagram will aid in understanding how a colloidal particle can be stabilized or conversely precipitated.

If the forces which tend to stabilize the dispersed particle are overcome then the particle can settle out. Since electrolytes contain both positive and negative charges they are effective in precipitating colloidal systems. As might be expected a salt having a highly charged ion of opposite charge to the colloidal particle is more effective than a salt having a small charge. For example, arsenious sulphide is a colloidal particle with a negative charge and should be acted on by the cation of a salt. Tests show that  $\text{Ba}^{++}$  cation is about 70 times as effective as  $\text{Na}^+$  cation in precipitating colloidal arsenious sulphide.

DIAGRAM SHOWING HOW A COLLOIDAL PARTICLE CAN BE STABILIZED OR PRECIPITATED.



Colloids can be prepared by two main methods, namely, **dispersion** methods and **condensation** methods. All dispersion methods are based upon breaking down of large particles until they reach the proper size range for the colloidal state. Dispersion methods are: mechanical disintegration, peptization, and electric arc. All condensation methods depend upon building particles up from molecular dimensions until they reach the colloidal state. The following are typical: reduction, formation in low ion concentration, and hydrolysis.

Purification of colloids can be brought about by **dialysis** and **ultra-filtration**. Dialysis is the process of allowing soluble crystalline materials to diffuse through a parchment membrane which holds back the colloid and effects a separation from true solutions. In order to effect a good separation fresh water should be passed over the dialyser to remove the electrolyte that has diffused through the membrane. If the dialysing chamber is placed between two electrodes the rate of diffusion of the ions is enhanced and the process is called **electrodialysis**.

In ultrafiltration the liquid medium as well as the electrolyte is removed from the colloid. Specially made filters of known pore size are used and pressure is applied to the solution. Ultrafiltration is useful in bacteriology in removing bacteria from solutions. Viruses, however, pass through the finest ultrafilters.

**Electrophoresis** is the process of causing charged lyophobic colloidal particles to move under influence of an applied electric potential through a solution. On the other hand **electro-osmosis** is the moving of the liquid medium under influence of an applied potential while the colloidal particles are immobile.

The term **gel** refers to a stiff semi-rigid precipitate, like gelatine, which retains the liquid in which it was originally dissolved. On standing gels undergo **syneresis**, that is, shrinkage with the loss of water. The temperature at which a gel liquefies or a liquid gels is affected by the presence of salts. **Hofmeister's lyotropic series** arranges anions of sodium salts in the order of their effect upon lowering the gelation temperature of a lyophilic colloid, thus :



That is to say NaSCN has the greatest effect upon lowering the gelation temperature of agar-agar and  $\text{Na}_2\text{SO}_4$  has the least effect.

The **isoelectric point** of a colloid is the concentration of hydrogen ion and other ions at which the particle has no net charge and under these conditions the system has its minimum stability, viscosity, and electrical conductivity.

The **gold number** is the concentration of lyophilic colloid which will just prevent a red gold colloidal solution from turning blue upon the addition of a definite amount of sodium chloride. The protective lyophilic colloid prevents the red gold particles from growing and becoming blue.

Colloids are very important in the living world. It has been said that the human brain is the most valuable colloid in the world. It is interesting to note that biologically an organism is dead when its protoplasm coagulates. Industrially colloids are of prime importance. Clouds and smokes are colloids cutting down the radiation reaching the earth, and causing dirt in cities which entails great financial loss as well as constituting health hazards to animals and plants. The Cottrell precipitator is used extensively to remove objectionable colloids from smoke in industrial centres. Proteins, dyes, soaps, cellophane, rayon, resins, plastics, and rubber are common industrial colloids.

**References :** *Colloid Science*, by Kraemer (Interscience Publishers, New York); *Treatise on Physical Chemistry*, by Taylor (D. Van Nostrand Co., New York); "Colloid Symposia," (*J. Physical Chemistry*, 1930-47); *Physical Properties of Colloidal Solutions*, by E. F. Burton (Longmans, Green and Co., New York); *Colloid Chemistry: Principles and Applications*, by Jerome Alexander (D. Van Nostrand Co., New York); *Surface Active Agents*, by A. M. Schwartz and James W. Perry (Interscience Publishers, New York); *Inorganic Colloid Chemistry*,

by H. B. Weiser (John Wiley and Sons, New York); *Reports on Colloid Chemistry and its Industrial Applications, 1917-1923* (British Association for the Advancement of Science); General Discussion on "The Physics and Chemistry of Colloids and their Bearing on Industrial Questions" (Faraday Society and Physical Society of London, Oct. 20, 1920); *The Chemistry of the Colloidal State*, by J. C. Ware (Chapman and Hall, London); Freundlich's *Capillary and Colloidal Chemistry* (Methuen and Co., London); *Chemistry of Colloids*, by R. Zsigmondy (Chapman and Hall, London); *Physics and Chemistry of Surfaces*, by N. K. Adam (Oxford University Press); *The Theory and Application of Colloidal Behaviour*, by R. H. Bogue (McGraw-Hill Book Co., New York); *Colloid Aspects of Food Chemistry and Technology*, by W. Clayton (J. and A. Churchill, London); *Colloid Chemistry, Theoretical and Applied*, edited by Jerome Alexander (Reinhold Publishing Corp., New York); *Surface Chemistry*, by E. K. Rideal (Cambridge Univ. Press); *Colloid Systems*, by A. von Buzách (Technical Press, Ltd., London); *Modern Colloids*, by R. B. Dean (D. Van Nostrand Co., New York); *Surface Chemistry*, Faraday Society Report (Interscience Publishers, New York); *Surface Chemistry for Industrial Research*, by J. J. Bikerman (Academic Press, New York); *The Theory of Emulsions and their Technical Treatment*, by W. Clayton (Churchill, London); *Colloidal Phenomena*, by Ernst A. Hauser (McGraw-Hill Book Co., New York); *Colloid Science, A Survey*, by H. R. Kruyt, editor (Elsevier Publishing Co., New York and London); *Colloid Science*, by A. E. Alexander and P. Johnson (Oxford Univ. Press); *Colloid Science*, by James W. McBain (Reinhold Publishing Corp., New York); Aerosols, Dialysis, and Emulsions.

**COLLOID MILL** — A machine for producing very fine dispersions of solid or liquid substances in liquid media. Colloid mills are used for such purposes as dispersing pigments in oil, suspending powdered coal in fuel oil, preparing paper pulp, and producing bitumen emulsions, mayonnaise, or pharmaceutical creams and ointments.

Size reduction in colloid mills is effected by either impact or shear (see Crushing and Grinding). The original Plauson colloid mill was of the impact or beater type, but modern machines usually rely upon shear. In a common type of mill, a mixture of liquid medium and the solid or liquid to be dispersed is caused to flow between two discs separated by a few thousandths of an inch, one disc being rapidly rotated while the other is stationary. The shearing surfaces may be either smooth, as in the Premier and Hurrell mills, or grooved, as in the Charlotte and Lancaster machines. With smooth surfaces very high speeds are necessary, up to 20,000 revolutions per minute in small mills. Machines with grooved surfaces can operate at lower speeds. In the Lancaster Disperser, hydraulic shear is intensified by internal recirculation of the charge, and there is no need for close mechanical clearances between the rotor and the stator.

If the material to be dispersed is a solid it must be pulverized before being fed to a colloid mill. There is no colloid mill that will satis-

factorily disperse a very hard substance, but such substances can be reduced to colloidal dimensions in the dry state by means of the "Microniser." (See Crushing and Grinding.)

A device which is not a true colloid mill, but which is used for emulsifying liquids in liquids, is the *Homogenizer*. It consists of a plunger pump which forces the mixed liquids through a spring-loaded valve. Hydraulic shear in the very small space between the valve and its seating causes one liquid to be finely dispersed in the other. (See Colloid State.)

**COLLOIDAL FUEL** — See Fuel (Colloidal).

**COLOCYNTH** — The dried fruit of a creeping plant known as the "bitter apple" (*Citrullus colocynthis*), growing chiefly on the shores of the Mediterranean and cultivated in Spain, Cyprus, Syria, and India. An extract made from the pulp is largely used in medicine as a purgative—either alone or in combination with other drugs. It contains as its active principle a very bitter purgative alkaloid and purgative resins.

**COLOPHONY** — See Gums and Resins.

**COLORIMETERS (Tintimeters)** — Instruments (such as "Lovibond's tintometer") used for making a comparison between the colours or depth of tint of a column of liquid with that of a prepared standard solution or with standard coloured glasses. There is a more scientific method based upon the measurement of the depth of the coloured solution required to absorb one-half or some other definite fraction of the light at three or four selected parts of the spectrum, such as red, yellow, green, and blue. The "B.D.H." capillator is an appliance claiming to provide an improved method for colorimetric determinations, while the Kodak Research Laboratories produce one by which all colours can be given an identification number, so that any required hue can be reproduced at any time. Instruments using a photo-electric cell are more accurate than those depending upon the human eye.

The definition of a colour is given by G. F. New, together with the measurements of radiations as determined by the "Guild" colorimeter in *B.C.A.*, B, 1933, 399.

*Reference: Photometric Chemical Analysis*, by J. H. Yoe (Chapman and Hall, Ltd., London).

**COLOURING MATTERS** — Natural colouring matters, such as cochineal, logwood, brazil-wood, safflower, saffron, etc., have been very largely replaced by the cheaper and more stable synthetic dyes, often of entirely different constitution, whereas others, such as indigo, alizarin, etc., have been superseded by chemically identical substances synthesized in the laboratory instead of being obtained from natural sources. (See Dyes, Lakes, Paints, and Plant Colouring Matters.)

**"COLSULANYDE"** — See Sulphanilamide.

**COLUMBITE (Niobite, Tantalite)** — A mineral of sp. gr. 5.25 to 6.5 and crystal system No. 4. (See Columbium.)

**COLUMBIUM** — Atomic weight 92.91. See Elements for other data. The International Union of Pure and Applied Chemistry has recommended (1949) the adoption of the name niobium to replace columbium. Columbium never occurs free in nature, but in a combined state commonly in minerals containing tantalum which are found in Sweden and certain parts of the United States. Columbite and tantalite are the principal ores from which the metal is extracted. Other important columbium bearing minerals are hatchettolite and fergusonite.

Metallic columbium can be produced either by thermal vacuum reduction of the oxide with carbon or by aluminothermic reduction. Another method is the electrolytic reduction of the fluoride in a fused bath. (See *Rarer Metals*, by J. DeMent and H. C. Dake (Chemical Publishing Co., Brooklyn, N. Y.)) The pure metal has a grey colour and bright lustre. It is malleable, ductile, and about as hard as wrought iron. It burns in air at its melting temperature when in a finely divided form. It is not affected by most acids, but is attacked by fused alkalis and by chlorine at elevated temperatures.

Classified not long ago as a rare metal, columbium now plays a very important part in metallurgy as a trace element. When added in minute amounts to stainless steels, it retards intergranular corrosion and extends the serviceability of these steels to temperatures exceeding 800° C. Columbium is also used in making chemical equipment and in welding rods for joining stainless steel. The metal appears to have some suitable applications for jewellery and tableware.

The compounds of columbium are very much like those of tantalum. The **oxides**  $\text{CbO}$  and  $\text{CbO}_2$  are dark powders, and the pentoxide ( $\text{Cb}_2\text{O}_5$ ) is white. The dioxide is soluble in hydrochloric acid and the pentoxide dissolves in sulphuric acid, ignition decreasing its solubility. There are two **chlorides**, namely,  $\text{CbCl}_3$  and  $\text{CbCl}_5$ .  $\text{CbCl}_3$  is rapidly oxidized in solution by oxygen. At red heat the pentachloride decomposes into the trichloride. The metal reacts with hydrogen upon heating to form the **hydride** ( $\text{CbH}$ ), which burns rapidly in air, and is not attacked by acids; the metal also forms a **nitride** ( $\text{Cb}_3\text{N}_6$ ) when heated to 1,200° C. with nitrogen. Potassium **hexacolumbate** ( $\text{K}_8\text{Cb}_6\text{O}_{19} \cdot 16\text{H}_2\text{O}$ ) is soluble in water. (See C. W. Balke in *Ind. Eng. Chem.*, 27, 1166 (1935).)

**COLZA OIL** — See Rape-Seed Oil.

**COMBUSTION** — The amount of heat given out by the combustion of a substance, whether rapid or slow, is the same when the product or products are identical, and is usually expressed in calories per gram-atom or gram-molecule, in calories per gram, or in B.Th.U. per pound. When carbon, for example, is burned into carbon dioxide, the heat of combustion of 12 grams is 97,050 calories, or 8,080 calories per gram, or 14,544 B.Th.U. per pound. (See W. A. Bone on "Forty Years of Combustion Research" (*J.S.C.I.*, 52, 202 T (1933)); *Gaseous Combustion at High Pressures*, by Bone, Newitt and Townend (Longmans, K.C.E.—9

Green and Co., London); *The Theory and Practice of Combustion*, by Lister and Harris (E. Benn, Ltd., London); *The Third Symposium on Combustion and Flame and Explosion Phenomena* (Williams and Wilkins, Baltimore); *Explosion and Combustion Processes in Gases*, by Wilhelm Jost (McGraw-Hill Book Co., New York and London); *Fuels and Their Combustion*, by R. T. Haslam and R. P. Russell (McGraw-Hill Book Co., New York); *Combustion, Flames and Explosions of Gases*, by Bernard Lewis and G. von Elbe (Macmillan Co., New York); also Air, Detonation, Explosives, Flames, Fuels, Gases, Ignition, Organic Analyses, Oxidation, and Steam.)

**COMMODITIES** — The annual *Commodity Year Book*, published by Commodity Research Bureau, Inc., New York, is a valuable reference containing statistical tables and charts showing for many commodities their prices, supplies, and distribution.

**COMPRESSIBILITY FACTOR** — A measure of the deviation of actual gases from the ideal gas laws, defined by the relation:  $PV = zRT$ , where  $z$  is the Compressibility Factor. For ideal gases  $z = 1$ . At pressures well below the critical the Compressibility Factor of a gas is approximately equal to its Activity Coefficient. W. K. Lewis and C. D. Luke (*Ind. Eng. Chem.*, **25**, 725 (1933)) give curves of compressibility factors for hydrocarbons. K. M. Watson and R. L. Smith (*National Petroleum News*, July 1, 1936) plot generalized compressibility factors for gases, derived from the Theorem of Corresponding States. J. Schmidt (*Bull. Assoc. Français des Tech. de Petrole*, March 1, 1939, p. 11) gives a single curve for saturated hydrocarbon vapours. (See Fugacity.)

**COMPRESSIVE STRENGTH** — See Strength (Compressive).

**CONCENTRATION** — The amount of any substance, expressed in any convenient units, present in unit weight or volume is called the concentration of that substance. Most commonly applied to solutions, the concentration may then be expressed in several different ways as follows:

(1) *Weight-Weight*. These concentrations are not affected by change of temperature.

(a) The weight of solute—the dissolved substance, say salt—in a given weight of solvent—the dissolving substance, say water. For example, sea water contains approximately 3.6 grams of salt per 100 grams of water.

(b) The percentage composition is given as the weight of solute per 100 grams of solution, *i.e.*, a 20 per cent. sodium chloride solution contains 20 grams of sodium chloride in 100 grams of solution (80 grams of water and 20 grams of salt).

(c) A **molal** solution contains one gram molecular weight of solute per *one thousand grams of solvent*. This solution is useful in physical chemistry because it sets up a fixed ratio of solute molecules to solvent molecules for each solvent. For example, in water solutions all 1 molal solutions contain one gram mole of solute per 55.5 gram moles of solvent. If sodium chloride of molar weight 58.5 is the solute, then

1 gram mole of same is 58.5 grams ; for water of molar weight 18 as solvent then  $\frac{106}{18} = 5.9$  gram moles.

(2) *Weight-Volume*. The weight of solute per unit volume of solution.

(a) A **molar** solution contains one gram molecular weight of solute per *one litre of solution*. For example, a one molar solution of sodium carbonate contains 106 grams (one gram mole) of  $\text{Na}_2\text{CO}_3$  in enough water to make 1 litre of solution.

(b) A **normal** solution contains one gram equivalent weight (see Chemical Compounds) of solute per *one litre of solution*. For example, 53 grams of sodium carbonate with enough water to make one litre of solution would be one normal, since 106 grams (1 gram mole)  $\div$  valence of 2 for  $2\text{Na}^+$  or  $1\text{CO}_3^{--}$ .

(c) Specific gravity-percentage composition by weight is also a weight-volume concentration. For example, a hydrochloric acid solution of sp. gr. 1.10 and 20 per cent. by weight contains 220 grams of hydrogen chloride in one litre of solution (or 1,100 grams of solution).

(3) *Volume-Volume*. This concentration is used mainly for gases and is the percentage by volume of each gas in a mixture of gases. For example, a sample of air contains 20 volume per cent. of oxygen and 80 volume per cent. of nitrogen.

(4) *Mole Fraction*. The ratio of the number of moles of one component of a solution to the total number of moles of all the components in say a solution. For example, a solution contains 30 grams of sodium chloride, 20 grams of sodium carbonate and 900 grams of water. The mole fraction of sodium chloride is

$$\frac{30}{58.5} \div \left( \frac{30}{58.5} + \frac{20}{106} + \frac{900}{18} \right), \text{ and of sodium carbonate } \frac{20}{106} \div \left( \frac{30}{58.5} + \frac{20}{106} + \frac{900}{18} \right)$$

(5) *Standard Solution*. Any solution whose concentration is definitely known is called a standard solution.

**CONCRETE** — Many varieties of concrete are made, but the constituents are always cement, a fine aggregate (usually sand) and a coarse one (usually pebbles or broken stones or breeze), the purpose of the fine material being to save cement by filling up more closely the pore spaces.

Experience has shown that the strength secured from the cement used is largely dependent upon the quantity of mixing water (varying from 5.5 to 7.5 gallons per bag of cement), according to the strength required, the size and grading of the aggregate determining the amount of water to be used.

It is claimed that the chemical action of "Ciment Fondu" is so rapid that when once the "initial set" has taken place the concrete made with it becomes warm and can therefore be laid in severe frosty weather. If the gauging water freezes after the "initial set" has occurred, the expansion of ice crystals forces the young crystals apart, and they will not reunite, so that the concrete has no strength and is ruined.

For rapid work, concrete is frequently mixed in a gravity machine or some similar device and tamped in a very fluid condition. A comparatively dry mixture rammed hard for a long time will give, when set, a dense mass, which will prove harder and less porous than a similar mixture lightly tamped with a larger quantity of water.

Concrete is largely employed in constructional work, road-making, also for making storage tanks for various oils, brine, and such other chemical liquids as have no action upon it. The imperviousness to water and resistance to chemical agents are largely dependent on the closeness of texture of the concrete. Among the various waterproofers used are fats, soaps, partly carbonated lime with aluminium and calcium soaps in aqueous paste form, and aluminium soaps and fats in admixture with paraffin oil. Concrete impregnated with injected molten sulphur is stated to be practically impervious, much stronger, and has found use in the construction of large electrolytic cells.

To get the best results, concrete should be allowed to set in a continuously moist state, and for this purpose calcium chloride in powdered form is advocated, using from 2 to  $2\frac{1}{2}$  lb. per square yard, on account of its deliquescent nature. Used also to the extent of some 3 per cent., it can be mixed with cement in the making to secure quicker hardening and increased compressive strength.

Reinforced concrete is made by embedding steel or other material to increase the strength; the deficiency of tensile strength of the concrete is compensated by the steel, the expansions and contractions effected by varying temperatures being for practical purposes identical.

There are several special varieties of sodium silicate, one of which contains 3.3 molecules of silica ( $\text{SiO}_2$ ) to 1 molecule of soda ( $\text{Na}_2\text{O}$ ) prepared for facing the surfaces of concrete so that the pores are filled to a depth of from  $\frac{1}{4}$  to  $\frac{1}{2}$  inch, thus giving an intensely hard outer layer. Fluosilicates of zinc and magnesium are also used in order to produce insoluble face products on the surface.

Blast-furnace slag can be employed as a substitute for gravel and sand in making concrete.

"Spun" concrete compacted with centrifugal force is made for pipes subjected when in use to internal pressure, and thus to tensional stresses.

A light-weight concrete devised by Axel Eriksson (a Swedish architect) is made from cement and shale lime, to which is added a small quantity of aluminium or zinc powder. When placed in contact with water, hydrogen is generated and the mortar thus sets in a porous state. Mortar of 40 parts cement and 60 of lime, with a porosity of 75 per cent., is stated to harden into concrete weighing from 40 to 50 lbs. per cubic foot, and having after a few weeks a compressive strength of 350 to 400 lbs. per square inch. It resists weathering, and can be used in walls of 6 to 8 inches thickness in house construction of one and two stories, but is not suitable for chimneys. (See publications of the American Society for Testing Materials; G. Ross Robertson on "Boulder Dam" (*Ind. Eng. Chem.*, **27**, 242 (1935)); Cement, Chemical Plant, "Ferrocete," "Prodorite," and Sodium (Silicate).)

**CONDENSATION** — The condensation of two or more molecules into one, or the formation of a new substance by various classes of interaction, and attended generally with the separation of either water, alcohol, ammonia, or hydrochloric acid. Acetic anhydride is, for example, a condensed compound derived from acetic acid by the elimination of water:  $2\text{CH}_3\text{COOH} - \text{H}_2\text{O} = (\text{CH}_3\text{CO})_2\text{O}$ . Among condensation reactions are those known as the "Aldol," "Claisen's," "Friedel-Crafts," and "Grignard." (See "Friedel-Crafts" Reaction, Formaldehyde, and Gums and Resins (Synthetic).)

**"CONDENSITE"** — A synthetic product prepared from phenol and formaldehyde. (See "Bakelite," and Gums and Resins (Synthetic).)

**CONDUCTOMETRIC TITRATIONS** — See Volumetric Analyses.

**CONDUCTION** — See Heat Transfer.

**CONGELATION** — The solidification of liquids by cooling or freezing.

**CONGO RED** — Prepared from tetrazotized benzidine and naphthionic acid. Used as a dye and as an indicator in chemical analysis. (See Dyes.)

**CONGO RESIN** — See Gums and Resins (Copal).

**CONIFERIN** — See Glycosides.

**CONIINE (Conine)** — See Hemlock.

**CONSOLUTE** — Term descriptive of liquids perfectly miscible in all proportions.

**CONSTANTS (Physico-Chemical)** — Determined values of chemical substances, such as atomic weights, vapour densities, specific gravities, melting- and boiling-points, the saponification and iodine values of fats and oils, etc. The physical and chemical constants of chemical entities depend, not only on their chemical purity, but naturally upon the peculiar physical form in respect of which such determinations are made. For example, the densities of pure white and grey tin respectively are 7.31 and 5.75. Again, Baker has demonstrated the variability of the boiling-points of many fluids, according to the duration of intensive drying to which they have been exposed, so that many so-called constants have to be accepted with careful understanding. (See intensive drying under heading of Heat; *Physical and Chemical Constants*, by Kaye and Laby (Longmans, Green and Co., London); and *International Critical Tables* (McGraw-Hill Book Co., New York); and various handbooks of chemistry, physics, and engineering.)

**CONTACT ACTION** — See Catalysis.

**CONTROL** — The regulated supply and removal, that is, control, of materials and energy is essential to the smooth operation of most industrial chemical processes. Equipment is frequently specialized in the hands of expert producers. See "Symposium on Measurement and Control in Chemical Industries" in *Transactions of the American Institute of Chemical Engineers*, 29, 211 *et seq.* (1933), and "Symposium on Automatic Control" in *Ind. Eng. Chem.*, 29, 1209 *et seq.* (1937).

**CONVECTION** — See Heat Transfer.

**CONVOLVULIN** — A resin, possibly containing glycosides, present in the tuber of *Convolvulus schiedanus* and possessing purgative properties. It is also present as the ether-insoluble portion of Jalap resin. (See Jalap, and Gums (Scammony).)

**COOLANTS** — See Anti-Freezes.

**“COOPERITE”** — A proprietary non-ferrous alloy, containing zirconium, molybdenum, tungsten, silicon, and aluminium, stated to be very efficient for making machine tools, iron being replaced by nickel as a basic constituent for tool production.

**CO-ORDINATION** — A theory of the structure of molecules or, in other words, the arrangement of atoms in chemical entities resulting from the functioning of valencies—that is to say, the exercise of unsatisfied affinities. Molecules, to use the definition given by J. Main Smith, are regarded as “spatial complexes consisting of atoms closely bound to a central atom,” and these spatial considerations are regarded as affording an adequate explanation of general and optical isomerism. According to Werner’s theory of “residual valencies,” seven types of isomerism are possible. According to Lowry there are two types :

“ (1) Centric co-ordination, in which the principal factor is the formation of a shell of electrons round a metallic atom ; and

“ (2) Cyclic co-ordination, in which the principal factor is the development or completion of a conjugated ring system by the insertion of a metallic ion.”

In co-ordination compounds as in the case of purpureo-cobalt chloride ( $\text{CoCl}_2 \cdot 5\text{NH}_3$ ) $\text{Cl}_2$  (see Ammines) three types of chemical combination are discernible :—electrovalency between the cobalt atom and the two chlorine atoms outside the co-ordination sphere, covalency between cobalt and chlorine within this sphere, and co-ordinate links between cobalt and five ammonias within the co-ordination sphere. (See *Chemistry of the Inorganic Complex Compounds*, by R. Schwarz (Chapman and Hall, London) ; Assymetry, Atoms, Bohr’s Theory, Chemical Affinity, Hydrogen Bonding, Isomerism, and Valencies.)

**COPAIBA OIL** — The volatile oil obtained by distillation of balsam of copaiba, in which it occurs to the extent of 60 to 90 per cent. (*Para Copaiba*) or 45 per cent. (*Muranham Copaiba*). It is colourless or pale yellow, of aromatic odour, miscible with alcohol, ether, etc. The chief and only well-defined constituent is the sesquiterpene caryophyllene ( $\text{C}_{15}\text{H}_{24}$ ). The oil has sp. gr. 0.895 to 0.918 at 15° C. ; ref. ind. at 20° C. 1.493 to 1.502 ; opt. rot.  $-4^\circ$  to  $-35^\circ$  according to variety. It was formerly used in medicine. (See Balsams (Copaiba).)

**COPAL GUM or RESIN** — See Gums and Resins.

**COPAL OIL** — A fatty oil (huile m’Pafu) from the Belgian Congo, stated to have a sp. gr. of 0.9165 at 19.5° C., sap. v. 196.2, and i.v. 59.5. It is non-drying, and likely to be of use for soap-making.

**COPPER (Cu) and its Compounds** — Atomic weight 63.54 (1947). See Elements for other data. There are about 240 copper-bearing minerals. Copper is found in nature in crystalline form (octahedra, crystal system No. 1); in large masses near Lake Superior (U.S.A.), and in some Siberian mines, while Katanga in the Belgian Congo ranks among the great producers. It also occurs in nature in the form of *copper pyrites* (*chalcopyrite*), a double sulphide of copper and iron ( $\text{Cu}_2\text{S} \cdot \text{Fe}_2\text{S}_3$ ), the Rio Tinto, Mason, and Barry ores being of this description. The Arizona deposits of ore contain up to 1.4 per cent. copper, and those of Utah about 1.1 per cent., and both are worked economically. Copper ore occurs in Australia and the Urals as *malachite*, a basic carbonate ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ); in Cuba as an oxide called *ruby ore* ( $\text{Cu}_2\text{O}$ ), also as *copper glance*, or sulphide ( $\text{Cu}_2\text{S}$ ), in Arizona, Nevada, and Cornwall; while the Chile ore of that description is associated with a valuable proportion of silver. *Azurite* (*chessylite*), a blue basic copper carbonate of sp. gr. 3.5 to 3.8, and a crystal system No. 5, occurs at Chessy near Lyons, and has the composition expressed by the formula  $2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ . *Atacamite*,  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ , a basic chloride of sp. gr. 3.75 to 4.3, is found in light green crystalline form (crystal system No. 4) in the district of Atacamite in Peru and elsewhere, while the green portion of the incrustation on Vesuvian lava has been given the same composition (G. Carobbi, *B.C.A.*, B, 1929, 289). *Olivenite* is a crystalline arsenate (crystal system No. 4, and sp. gr. 4.13 to 4.38) of the composition of  $4\text{CuO} \cdot \text{As}_2\text{O}_5 \cdot \text{H}_2\text{O}$ . *Berzelianite* is a copper selenide ore. *Brochantite*,  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ , and *antlerite*,  $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ , are two naturally occurring basic sulphates. *Tetrahedrite* or *grey copper ore* is a compound ore, containing the sulphides of copper and antimony with about 52 per cent. copper (crystal system No. 1, and sp. gr. 4.5 to 5.0). *Cuprite* is a red oxide ore of the composition  $\text{Cu}_2\text{O}$  (crystal system No. 1, and sp. gr. 5.8 to 6.2), and this, together with cupiferous pyrite, are the minerals most commonly found. These latter are converted into sulphates by oxidation, and are often concentrated by a leaching process in a zone of rich oxide below.

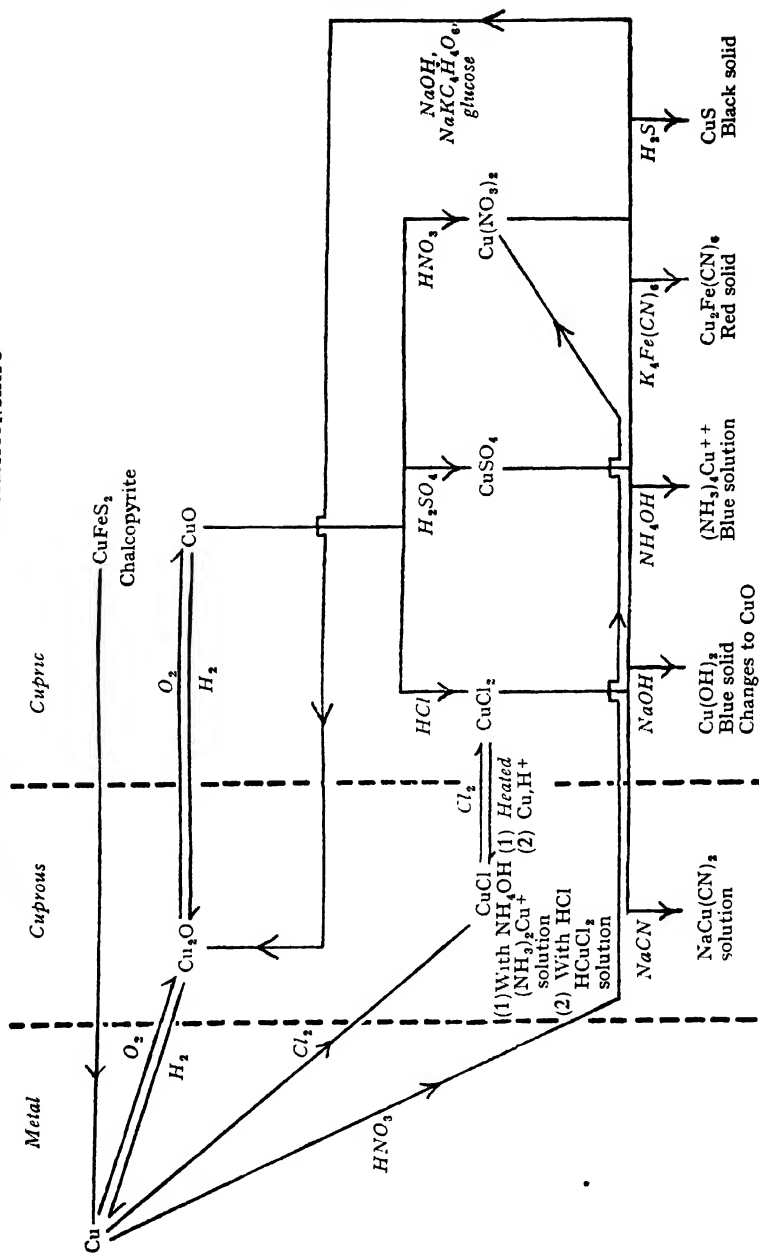
*Chalcopyrite* is found abundantly in the United States, and good concentrates are obtained from this mineral by the selective flotation process. Large deposits of copper ores containing from 3 to 5 per cent. occur in Northern Rhodesia.

*Copper Resources of the World* was prepared by the Sixteenth International Geological Congress, Washington, 1933.

**Metallurgy** — When the oxide of copper is used for production of the metal, it is smelted in a blast-furnace with coal or coke, by which it is reduced as shown by the equation:  $\text{Cu}_2\text{O} + \text{C} = \text{CO} + 2\text{Cu}$ ; that is to say, the oxygen of the cuprous oxide enters into combination with the carbon of the coal or coke, forming carbon monoxide, and the metallic copper thus produced is afterwards refined by other processes. With other ores of copper containing sulphides, the sulphur content is first of all lowered by roasting and reduction with carbon, whereupon part of the sulphur is removed as sulphur dioxide gas. The residual matte, which contains the copper, is discussed later.

Arranged by the Editor.

COPPER-CONTAINING SUBSTANCES  
CHART SHOWING PRINCIPAL INTER-RELATIONSHIPS



## COPPER, WORLD SMELTER PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country				Smelter Copper Metric Tons	Ore (Cu Content) Production where Markedly Different from Smelter Pro- duction Metric Tons
Belgium	..	..	..	90,000	None
Germany-Austria	..	..	..	70,000	30,000
Yugoslavia	..	..	..	40,000	
Finland	..	..	..	10,000	
*Spain	..	..	..	10,000	30,000
Norway	..	..	..	10,000	
Sweden	..	..	..	10,000	
United Kingdom	..	..	..	10,000	None
				<hr/> 250,000	
U.S.S.R.	..	..	..	100,000	
U.S.A.	..	..	..	700,000	620,000
*Canada	..	..	..	220,000	260,000
Mexico	..	..	..	40,000	
				<hr/> 960,000	
*Chile	..	..	..	350,000	370,000
Peru	..	..	..	40,000	
				<hr/> 390,000	
Japan	..	..	..	100,000	
*Cyprus	..	..	..	None	30,000
				<hr/> 100,000	
*Northern Rhodesia	..	..	..	210,000	250,000
Belgian Congo	..	..	..	130,000	
Union of South Africa	..	..	..	10,000	
				<hr/> 350,000	
Sum of above				2,150,000	
WORLD PRODUCTION				2,170,000	

\* Exporting country for ore.

There is a process for the extraction of copper from some of its ores by so-called ammonia leaching, in which the natural sulphide ores are roasted into oxides, and then treated with ammonia solution, thus producing a dark blue liquid which upon heating gives off ammonia gas and carbon dioxide gas, and deposits a heavy black powder consisting in the main of cupric oxide (CuO).

The "Lockwood" process for the electrolytic production of copper is one of separation and deposition of the metal from a pulp containing 9\*

the entire crushed ore with an acid solution, air being forced through the mixture to prevent sedimentation. If the ore be a sulphide, it must first of all be roasted to get rid of the sulphur. The dissolved copper is deposited on the cathode after running by gravity into an adjacent recovery tank, while the weakened acid is regenerated at the anode. It is stated that the time of treatment is so short that fouling materials such as iron do not dissolve in appreciable quantity.

The copper, which is contained (to the extent of about 3 per cent.) in burnt pyrites used in the manufacture of sulphuric acid, is extracted by a wet process in which the residual mass is calcined with salt, which converts the copper into the form of chloride, after which the fused mass is lixiviated with water and the copper precipitated from the solution by means of scrap-iron or by electrolysis. The metal so obtained in a spongy condition can either be smelted, or roasted into oxide, and sometimes the oxide so prepared is subsequently dissolved in sulphuric acid in order to produce cupric sulphate, which can be crystallized out from the solution.

The crude copper "matte," containing from 40 to 50 per cent. copper, obtained by the roasting and reduction processes, furnishes the crude material from which the "blister" copper is subsequently obtained by a remelting process, and this again is further refined by an electrolytic process which yields ingots of 99.9 per cent. purity as used for the metal-working industries. Almost all of the world's copper is now obtained electrolytically.

The *grades* of copper dealt with in Great Britain are "Best Selected" (B.S.), with an average content of 99.75; "Tough," "Tough Pitched," or refined copper containing 99.25 per cent.; "Electrolytic" (the purest of all) and "Standard," meaning any class containing not less than 97 per cent., including "Chile Bars." "White Metal" is a name for matte consisting almost entirely of copper sulphide.

**Verdigris** has frequently been described as a basic copper carbonate of the composition  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ , but the name is more properly given to basic cupric acetates, one such product having long since been manufactured at Montpellier (France) by exposing plates of copper to the air in contact with acetic acid or fermenting wine-lees. Another form styled "green verdigris" was made at Grenoble by periodically sprinkling copper plates with vinegar in a warm room. These products, which varied in composition with the different modes of procedure and other circumstances, are quite distinct from "Patina," the green copper compound so often occurring on copper surfaces exposed to the air, and particularly in towns where sulphurous fumes constitute ingredients. In the past, **patina** has been generally described as a form of basic copper carbonate, sometimes expressed as having the composition of malachite; but while it is certain that some kind of carbonate may be found under certain conditions, it has been demonstrated by W. H. J. Vernon that the green patina which forms on the surface of copper after prolonged exposure to the air consists under most conditions essentially of basic copper sulphate. At the sea-board it may consist essentially of basic copper chloride. It has also been shown that these open-air

corrosion products of copper tend to assume the chemical compositions of known minerals, such as *brochantite* ( $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ ), basic copper chloride like that of *atacamite* ( $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$ ), and basic copper carbonate like that of *malachite* ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ). (See Vernon, on "Artificial Production of Green Patina" (*Journal of the Institute of Metals*, 49, No. 2 (1932)).

**Uses** — Copper is one of the most useful metals; has a reddish colour, is rather hard but flexible, tenacious, very ductile and malleable, and, apart from its employment in the form of wire for telegraphic purposes (on account of its excellent conductivity), is largely used for making domestic utensils, coins, sheathing of wooden ships, alloys with cadmium, zinc, and other metals, while with various proportions of tin it forms *bronze*, *bell-metal*, *gun-metal*, *brass*, and "*Muntz metal*." An alloy of copper and aluminium of golden colour named "*Alcobronze*" is stronger, tougher, and harder than any other known bronze, and capable of resisting the influence of air, acids, and salt water. "Wrought Copper Base Alloys" are described by D. K. Crampton (*Ind. Eng. Chem.*, 28, 1397 (1936)). (See Alloys.) It is weldable by the so-named "Premag Process." Formerly the welding of copper was practically impossible, or at least most unsatisfactory, but it has now been achieved by means of slight modifications in the technique of welding non-ferrous metals by the use of copper alloy filler rod and flux of an appropriate type.

The catalytic action of reduced copper varies according to its mode of formation, serving among other processes as a catalyst for the oxidation and dehydration of menthol.

**Copper Oxides** — There are two important oxides of copper, both insoluble in water, namely, the red cuprous oxide ( $\text{Cu}_2\text{O}$ ), which is found native as *cuprite*, and gives to glass a beautiful ruby coloration; and cupric oxide ( $\text{CuO}$ ), which is black and produces blue and green salts by combination with acids. Cuprous oxide suspended in water made alkaline with sodium hydroxide is rapidly converted into cupric oxide by the passage of air. Cupric oxide in the precipitated form is useful as a catalytic agent, also in compounding anti-fouling compositions and paints for ships.

There are a number of **copper hydroxides**. A solution of the blue hydrated cupric oxide or cupric hydroxide ( $\text{Cu}(\text{OH})_2$ ) (as made by interaction of an alkaline hydroxide and solution of a copper salt) dissolved in ammonia is used in the preparation of "Willesden paper" and some silk substitutes, while the hydroxide itself, which is insoluble in water, is used as a pigment.

**Copper Chlorides** — There are two chlorides of copper corresponding to the two oxides, used as mordants, etc. The cuprous chloride ( $\text{Cu}_2\text{Cl}_2$ ) is white and insoluble in water, whereas the cupric chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) is blue-green and soluble to form a green (when concentrated) or blue (when dilute) solution.

**Cupric Nitrate** — A soluble crystalline salt, which has the composition  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and is used in the paper industry and ceramics.

**Cupric Sulphate (Blue Vitriol, Blue Copperas)** ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) — This

important salt of copper occurs naturally as *chalcanthite* in some Chilian mines, Arizona, and elsewhere, and is formed when the metal or its oxide is dissolved in sulphuric acid :  $\text{Cu} + 2\text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$  (hot concentrated acid);  $\text{CuO} + \text{H}_2\text{SO}_4 = \text{CuSO}_4 + \text{H}_2\text{O}$  (dilute acid). As prepared by the leaching of copper ores with sulphuric acid, the product requires purification from ferrous and ferric sulphates and other impurities. It is soluble in water, and the solution yields by crystallization fine blue crystals containing 5 molecules of water. Its dehydration is the subject of a paper by Garner and Tanner (*J.C.S.*, 1930, 47). It is used as a mordant in dyeing, in the manufacture of "Scheele's green," "Brunswick green," and other pigments, in electric batteries, and in preparing a number of compounds used for the destruction of snails and slugs, and low forms of insect pests on vines and other plants. A preparation sometimes used to combat these insect pests is a 2 per cent. solution in lime water. (See Bordeaux Mixture.) In addition to the two natural basic sulphates, others have been described, including one of the composition  $4\text{CuO} \cdot \text{SO}_3 \cdot 4\text{H}_2\text{O}$ .

**Copper Sulphides** — There are two sulphides of copper corresponding to the two oxides: cuprous sulphide ( $\text{Cu}_2\text{S}$ ), chemically identical with the mineral known as crystalline *copper glance*; and cupric sulphide ( $\text{CuS}$ ), chemically identical with the mineral *indigo copper*. Both are used as protective paints on ships.

**Scheele's Green** ( $\text{CuHAsO}_3$ ) (sometimes described as copper hydrogen arsenite) is of bright green colour, and used as a pigment and insecticide. It is made by mixing solutions of cupric sulphate and sodium arsenite, or by dissolving arsenious oxide ( $\text{As}_2\text{O}_3$ ) in potassium carbonate solution and adding to it a solution of copper sulphate in water. Its composition is said to vary with the method of preparation. According to one report, Scheele's green is a neutral hydrous copper arsenite of the formula  $3\text{CuOAs}_2\text{O}_3 \cdot \text{H}_2\text{O}$ , and not  $\text{CuHAsO}_3$ . It differs from emerald green in not containing any copper acetate. (See Paris Green, below.)

**Brunswick Green** is a pigment (copper oxychloride) made by moistening copper turnings with a solution of ammonium chloride (sal ammoniac), and exposure to the air.

**Paris Green** (Schweinfurt Green) — Copper acetoarsenite, represented by the formula  $3\text{CuOAs}_2\text{O}_3 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ , is an emerald-green pigment prepared by boiling basic acetate of copper with arsenic trioxide. It may also be prepared by mixing verdigris with a solution of arsenious acid acidified with acetic acid, but is ordinarily made by adding sodium arsenite and sodium acetate to an acetic acid solution of copper sulphate. It is used as an insecticide for spraying fruit trees infested with caterpillars and the larvæ of "leather jackets."

**Emerald Green** — A pigment that is a combination of metarsenite and acetate of copper of the formula  $3\text{Cu}(\text{AsO}_2)_2 \cdot \text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$ .

**Cupric Acetate** ( $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ ) — A greenish-blue crystalline body, soluble in water and alcohol, which finds employment as an insecticide, in ceramics, in preparing ships' bottoms composition, and in printing fabrics.

**Copper Basic Acetate** — Prepared as mentioned previously by exposure of copper metal to air in contact with acetic acid or vinegar.

**Copper Borate** — A crystalline substance soluble in water ; used as a pigment.

**Copper Carbonates** — Two carbonates are known, one of which is identical in composition with native *malachite* ( $\text{CuCO}_3, \text{Cu}(\text{OH})_2$ ), and another identical with *azurite* ( $2\text{CuCO}_3, \text{Cu}(\text{OH})_2$ ), both of which are insoluble green powders used not only as pigments and as driers in oil-boiling, but also as insecticides (by dry spraying). A stable basic carbonate is formed by the intermixture of a cupric salt and a soluble carbonate.

**Cupric Chlorate** ( $\text{Cu}(\text{ClO}_3)_2, 6\text{H}_2\text{O}$ ) — A bluish-green, deliquescent, crystalline body, soluble in water (of dangerous character, like most chlorates) ; used as a mordant.

**Cupric Cyanide** ( $\text{Cu}(\text{CN})_2$ ) — A green powder, insoluble in water (of dangerous character through evolution of poisonous cyanogen gas) ; used in metallurgy.

**Cupric Fluoride** ( $\text{CuF}_2, 2\text{H}_2\text{O}$ ) — A blue, crystalline salt, soluble in water ; used in ceramics and enamels.

**Cuprous Phosphide** ( $\text{Cu}_3\text{P}_2$ ) is a dark, insoluble, metallic-looking powder ; used in making phosphor bronze.

**Cupric Resinate** is a green compound soluble in ether and oils, used as a metal paint, particularly for ships' bottoms.

**Copper Ammonium Sulphate (Ammonio-Cupric Sulphate)** ( $\text{CuSO}_4, 4\text{NH}_3, \text{H}_2\text{O}$ ) — A blue, crystalline, soluble salt ; used in calico printing and as an insecticide.

**Copper Chromate** — A basic insoluble compound ( $\text{CuCrO}_4, 2\text{CuO}, 2\text{H}_2\text{O}$ ) of chocolate colour ; used in dyeing.

**Ammonio copper** ions are formed by excess of ammonium hydroxide on both cupric and cuprous salts. The former yield the deep blue solution frequently used in the identification of  $\text{Cu}^{++}$  ion, and is  $(\text{NH}_3)_4\text{Cu}^{++}$  ; the latter a colourless solution (but usually accompanied by some of the blue) of  $(\text{NH}_3)_2\text{Cu}^+$  commonly used as a reagent to absorb carbon monoxide from gases (from which carbon dioxide and oxygen have been previously removed).

The salts of copper are poisonous. The soluble salts give a characteristic blue colour in dilute water solution. Copper compounds, when moistened with hydrochloric acid and held in a flame on a clean platinum wire, show green flame coloration.

**COPPER GLANCE** — See Copper Sulphides, and Redruthite.

**COPPER-ZINC COUPLE** — An appliance consisting of zinc and precipitated copper deposited thereon, which was used by Gladstone and Tribe in preparing methane from methyl iodide and in the study of a variety of other chemical changes induced by the couple.

**COPPERAS (Blue)** — Common name for cupric sulphate.

**COPPERAS (Green)** — Common name for ferrous sulphate.

**COPRA** — The dried edible kernel of the common coconut, as prepared for the extraction of coconut oil, of which it contains, when dry, up to 66 per cent. Copra-meal is stated to be rich in the amino-acids necessary for the maintenance of growth, and when mixed with green leaves furnishes a fairly perfect food for pigs. (See Coconut Oil.)

**COPROLITES** — Imported phosphatic deposits in the nature of extinct animal excrements found in certain geological formations, particularly in the *lias*. They consist chiefly of calcium phosphate and carbonate, the phosphate amounting in some cases to as much as from 80 to 90 per cent., and on account of their phosphatic character they are valuable fertilizers. (See Apatite, Guano, Phosphorus, and Superphosphate.)

**COQUILHO (COQUILLA) NUTS** — This Brazilian nut (from *Attalea funifera*), which is of large size and used by button makers, possesses a kernel which is stated to yield about 65 per cent. of a non-drying oil, having i.v. 14 and sap. v. of 261.

**CORAL** — A calcareous substance containing from 95 to more than 98 per cent. calcium carbonate, 0.28 to 0.84 calcium phosphate, and from 1.64 to 3.8 per cent. water and organic matter, forming the hard skeleton of many varieties of some five kinds of organisms: *Actiniozoa*, forming the principal constituents of coral reefs; *Hydrozoa*, characteristic of the larger common corals known as millepores; *Bryozoa*, found in the more delicate corals; *Foraminifera*; and *Nullipores*.

“**CORAMINE**” — See Nikethamide.

**CORDITE** — See Explosives.

“**CORDURA**” (Du Pont) — Trade-mark for a viscose process yarn of higher strength than normal rayon.

**CORIANDER OIL** — A volatile oil obtained by distillation from the fruit of *Coriandrum sativum*, indigenous to Southern Europe and cultivated in England, U.S.S.R., Hungary, Northern Africa, and India. The seeds contain from 0.2 to 1 per cent. of essential oil which is a colourless or pale yellow liquid having a characteristic aromatic odour and taste and is used in medicine as a flavouring agent and carminative; soluble in alcohol and ether; sp. gr. 0.870 to 0.884 at 15° C.; opt. rot. +8° to +13°; ref. ind. 1.462 to 1.472 at 20° C. A description of Rumanian coriander oil is given by E. Kopp in *B.C.A.*, B, 1930, 120, and the composition of samples from various sources by Ramstad in *Chem. Abs.*, 38, 218 (1944).

**CORK** is the outer bark or cork of the *Quercus suber* tree, which grows in the southern part of Europe, the north of Africa, and in the East, and consists in part of a modified form of cellulose (about 22 to 23 per cent.). The perfected cork is not produced until the tree is from 50 to 60 years old. Gatherings are made every 8 or 10 years after the tree is 20 years old. According to F. Zetzsche and G. Rosenthal, suberin is the essential constituent of cork. When oxidized with nitric acid cork yields, amongst other products, oxalic acid. Its specific gravity ranges from 0.215 to 0.24, and increases with age. Cork dust is used in making linoleum and oilcloth coverings.

**CORNELIANS (CARNELIANS)** (Crystal system No. 3) — Beautiful variegated quartz stones of the finer varieties of chalcedony, found chiefly in India. (See Chalcedony.)

**CORNETITE** — The name of a basic phosphate of copper occurring in Northern Rhodesia, and applied also to a basic double phosphate of cobalt and copper found at Katanga (Belgian Congo).

**CORN OIL** — See Maize Oil.

**CORNIN** — See Glycosides.

' **CORONDITE** ' — An abrasive containing crystals of alumina, made by smelting red bauxite with anthracite, and blowing air through the mixture.

" **CORONIUM** " — A bronze alloy of copper 16 parts, zinc 3 parts, tin 1 part, of which tensile tests have given from 16 to 18 tons per square inch.

**CORPUS LUTEUM** — A buff or light brown powder, consisting of the dried corpus luteum, deprived of ovarian substance, obtained from cattle or swine. The corpus luteum is a body consisting of large, glandular cells containing granules, which is formed in the female ovary after the mature ovum has been released by rupture of the Graafian follicle. It secretes a hormone, progesterone, which is responsible for causing the proliferation of the internal epithelium of the uterus and for the maintenance of pregnancy. The dried substance was formerly used in medicine but has now been largely replaced by preparations of the pure hormone or ethisterone, both of which are prepared synthetically. The physiology of the corpus luteum is reviewed by Corner, *J. Amer. Med. Assoc.*, **116**, 591 (1941). (See Ethisterone, Oestrone, Progesterone, and Testosterone.)

**CORROSION** — The corrosion of metals is of two general types: direct chemical attack by non-electrolytes, and electrochemical action in the presence of electrolytes. Examples of the first type are the action of oxygen and hydrogen sulphide on steel at high temperatures. Practical corrosion problems are usually of the second type. Many substances which do not corrode a given metal when perfectly dry become corrosive in the presence of even traces of water, when electrochemical forces come into play.

Electrochemical corrosion occurs where conditions are such that an area of metal becomes the anode of a short-circuited electrolytic cell. The cell may consist either of two dissimilar conductors in contact with one another and with the same electrolyte, or of two dissimilar electrolytes in contact with one another and with the same metal. The general rules are: (a) in the first or galvanic type of cell, the more electropositive element becomes the anode and corrodes (for the relative polarity of metals, see Electricity (Electromotive Series)); (b) in the second or concentration type of cell, corrosion attacks the area of metal which is in contact with the more dilute electrolyte. A rolled steel plate with fragments of mill scale ( $\text{Fe}_3\text{O}_4$ ) upon its surface and

immersed in a saline solution affords an example of galvanic corrosion ; metallic iron is electropositive to the oxide, and therefore the metal surrounding each particle of scale becomes anodic and is attacked. Crystals of free graphite in cast-iron can set up a similar type of corrosion. Action due to concentration differences is exemplified by a deep iron tank containing a salt solution which is exposed to the air and not stirred. The concentration of dissolved oxygen is higher near the surface than deeper down ; consequently the metal at the bottom of the tank becomes anodic and tends to corrode. A localized concentration cell is also set up at the waterline, the iron in contact with the meniscus being cathodic while that just below the surface is anodic. Hence an open iron tank containing an unstirred aqueous solution tends to corrode in two distinct regions ; round the waterline and near the bottom. Waterline corrosion is particularly severe when the liquid level fluctuates.

Where a metal is severely attacked with evolution of hydrogen, *e.g.*, iron in hydrochloric acid or aluminium in sodium hydroxide, numerous microscopic cells are set up at the metal/liquid interface. A given small area of metal may be anodic at one moment and cathodic at another, so that attack is substantially continuous over the whole surface. The minute electrolytic cells responsible for this type of corrosion are believed to be caused by momentary differences in hydrogen overvoltage.

Given the basic conditions for electrochemical corrosion, the rate at which a particular metal is attacked by a particular solution depends upon specific factors, among which are the magnitude of the potential difference set up, conductivity and  $pH$  value of the electrolyte, solubility of the corrosion products, and hydrogen overvoltage. The rate at which iron and steel are attacked increases with the acidity of the solution and its dissolved oxygen content.

The mechanism by which other metals corrode is similar in principle to that described for iron and steel. Highly electro-negative metals such as gold and platinum are seldom subject to electrochemical corrosion because they are nearly always cathodic to other materials. The rate at which base metals corrode depends largely upon the nature and solubility of the corrosion products. Some metals, such as aluminium and chromium, form a very thin but firmly adherent film of insoluble oxide which protects the underlying metal and greatly retards any further attack. Stainless steel depends for its corrosion resistance upon a similar oxide film. U. R. Evans has succeeded in isolating these oxide films by carefully dissolving away the base metal. The thickness and protective value of an oxide film may sometimes be increased by suitable treatment, *e.g.*, in the blueing of steel, or the anodizing process for aluminium.

The protective value of dipped and plated metallic coatings depends largely on the electrochemical potential of the coating with respect to the base metal. Zinc is electropositive to iron, and hence if a galvanized iron surface is scratched so as to expose the iron, it is the zinc coating which dissolves while the iron is protected from corrosion.

Copper-plating on iron has the opposite effect. Copper is electro-negative to iron, and consequently if a small area of iron becomes exposed, corrosion is concentrated on that area and a deep pit may rapidly develop. The rate at which corrosion penetrates is inversely proportional to the area of metal which is anodic; a very small anodic region combined with a large area of cathode is therefore a source of particular danger.

The corrosion of a given metal by a given solution is affected by many external factors such as temperature, degree of aeration, depth of immersion, fluid velocity and turbulence, and stresses in the metal. For this reason it is usually wise, before choosing a corrosion-resistant material for a particular duty, to carry out practical tests under something like service conditions.

For the corrosion resistance of particular metals and alloys, see also Materials of Construction, and Stress Corrosion.

#### SOME CASES OF PROTECTIVE ACTION

Positive and Corroded	Negative and Protected
Magnesium	Zinc; iron; lead; copper
Aluminium	Aluminium (99.2%) alloy "2S"; cadmium
Zinc	Iron; cast iron; steel
Chromium	Iron-chromium (13%) alloy; nickel
Iron	Iron-chromium (18%)-nickel (8%) alloy "18-8-S"
Cadmium	Hastelloy C (Ni-Fe-Mo)
Cobalt	Lead; copper
Nickel	Lead; copper
Tin	Hastelloy A (Ni 60%, Fe 20%, Mo 20%)
Lead	Brass; bronze; copper; copper-nickel alloy

*References:* H. H. Uhlig, *Corrosion Handbook* (John Wiley and Sons, New York); F. N. Speller, *Corrosion: Causes and Prevention* (McGraw-Hill Book Co., New York); U. R. Evans, *Metallic Corrosion, Passivity and Protection* (Longmans, Green and Co., New York); U. R. Evans, *An Introduction to Metallic Corrosion* (E. Arnold and Co., London); R. J. McKay and R. Worthington, *Corrosion Resistance of Metals and Alloys* (Reinhold Publishing Corp., New York); Florence Fenwick and John Johnston, "Steels Resistant to Scaling and Corrosion" (*Ind. Eng. Chem.*, **28**, 1374 (1936)); *Pipe Corrosion and Coatings*, by Erick Larson (American Gas Journal, New York); *Bibliographic Survey of Corrosion—1945* (National Association of Corrosion Engineers, Houston, Texas).

**CORROSIVE SUBLIMATE** — See Mercuric Chloride.

**CORTISONE (Compound E)** — A crystalline, steroid hormone isolated from the adrenal cortex, namely, 17-hydroxy-11-dehydrocorticosterone. It was first isolated in 1935 from extracts of the adrenal cortex by E. C. Kendall (see *J. Biol. Chem.*, **114**, 613 (1936), and *Proc. Mayo Clin.*, **24**, 298 (1949)). Until 1946, only small amounts of the substance were

available but it had been shown to improve muscle activity in rats subjected to adrenalectomy and to retard the growth of young rats (see Ingle and Kendall, *Proc. Soc. Exp. Biol. et Med.*, **45**, 602 (1940) ; Ingle and Kuizenga, *Endocrin.*, **36**, 218 (1945) ; and Kendall, *Arch. Path.*, **32**, 474 (1941)). It had also been shown to intensify the diabetic state of depancreatized rats (see Ingle and Thorn, *Amer. J. Physiol.*, **132**, 670 (1941) ; and Ingle, *Proc. Soc. Exp. Biol. et Med.*, **44**, 176 (1940)). In 1946, cortisone was synthesised in the Merck Laboratories by Sarrett, using desoxycholic acid, a bile acid, as the starting material. It has since been prepared and used in the form of its acetate and has proved to be valuable in the treatment of rheumatoid arthritis (see P. S. Hench, *Proc. Mayo Clin.*, **24**, 167 (1949) ; Hench, Kendall, Slocumb and Polley, *Proc. Mayo Clin.*, **24**, 181 (1949) ; and Boland and Headley, *J. Amer. Med. Ass.*, **141**, 301 (1949)).

“**CORUBIN**” — Slag produced in manufacturing chromium by the “Thermit” process, containing about 72 per cent. alumina and 13 per cent. chromium, used as an abrasive in lens grinding. (See Chromium.)

**CORUNDUM** — See Aluminium.

“**CORVOTONE**” — See Nikethamide.

**COTARNINE** ( $C_{12}H_{15}O_4N$ ) — A colourless, crystalline base obtained from the alkaloid narcotine by oxidation with nitric acid. It is sparingly soluble in water but more soluble in ether and alcohol ; m.p. 132 to 135° C. with decomposition. Used in medicine.

**COTTON** — The wool-like product of all the species of the genus *Gossypium* (N.O. Malvaceæ) made from the seeds, and consisting of from 90 to 95 per cent. cellulose. It is cultivated in many countries, including the U.S.A., East Indies, China, Uganda, Egypt, etc., the U.S.A. supplying upwards of one-half of the total production. Cotton seed contains on average 9 to 10 per cent. water, 20 to 23 per cent. oil, 18 to 21 per cent. albuminoids, 22 to 27 per cent. digestible carbohydrates, 17 to 26 per cent. woody fibre, and 4 per cent. mineral matter. The pressed cake has value as a feeding stuff. Cotton fabrics deteriorate in strength by exposure to heat (90° C.) partly as the result of oxidation, while the cellulose and other constituents (which vary in raw material of different origins) are subject to alteration or partial removal by the use of bleaching agents and other technical processes. The “hydrophile” power of cotton (wool) is the speed with which it becomes soaked, and the “absorptive” power is indicated by the weight of liquid retained after immersion under a small definite pressure.

Zinc chloride is largely used on account of its antiseptic property as an ingredient in cotton sizing, and, although other agents of greater antiseptic value are more or less available, their use in cotton dyeing is often attended with disadvantages in colour, cost, etc.

Among the constituents of the benzene extract of American and Egyptian cotton sliver, the principal one in the wax-like product thus obtained is an alcohol termed gossypyl alcohol ( $C_{30}H_{62}O$ ), m.p. 85° C. and it is accompanied by smaller proportions of montanyl alcohol

( $C_{28}H_{58}O$ ), m.p.  $83.5^{\circ}C$ . ceryl alcohol ( $C_{26}H_{54}O$ ), carnaiibyl alcohol ( $C_{24}H_{50}O$ ), and a mixture of phytosterols, together with free fatty acids, etc. According to one account, a thorough extraction with benzene yields 0.503 per cent. wax, and after treatment with acid further 0.058 per cent. Lecomber and Probert have shown the fat and wax content (carbon tetrachloride extract) of different cottons varies from 0.34 to 0.54 per cent., and average values of some twenty-seven samples are as follows: acid value 26, sap. v. 70, i.v. 23. The ash content ranges from about 1 to  $1\frac{1}{2}$  per cent.

Mergerized cotton fibre is obtained by dipping in sodium hydroxide solution and drying under tension. So-called "immunized" cotton is obtained by the partial etherification of cotton, and is characterized by its resistance to the usual type of substantive cotton dyestuffs; but by treatment of the product with ammonia an "amidated" variety is prepared which exhibits a remarkable affinity for acid dyestuffs.

*References:* *The Production of Cotton*, by H. G. Collings (Chapman and Hall, London); and *Chemistry of Cotton Cellulose*, by A. J. Hall (Ernest Benn, London); and Cellulose, Cotton-seed Oil, Linen, and Toluene Sulphonylchloride.

**COTTON-SEED BRAN** — The oxidation of this by-product with nitric acid under certain conditions is said to give a product consisting mainly of trihydroxyglutaric acid ( $COOH.(CHOH)_3.COOH$ ), intermediate between tartaric and mucic acids, which appears to be a satisfactory substitute for both tartaric and lactic acids in their applications in the textile industry.

**COTTON-SEED OIL** — This oil, expressed with the aid of heat from cotton seeds (*Gossypium herbaceum*), is largely used (after hardening) in making margarine and soaps, and in its natural form as a leather dressing and in preparing carron oil. Large amounts of cotton seed come from Korea and North China, which supply the Japanese mills. Supplies also come from Egypt, but the largest amount is produced in the U.S.A. The Egyptian variety yields about 22 per cent., the Indian about 16 to 18 per cent., the Chinese about 8.5 per cent., and the American about 13 per cent. of oil. Its ref. ind. is 1.4643 at  $40^{\circ}C$ ., sp. gr. 0.922 to 0.927, sap. v. 193 to 195, m.p.  $35^{\circ}$  to  $38^{\circ}C$ ., and i.v. 105. Cotton-seed oil is refined by steam-heating it with 5 per cent. of a 16° Baumé caustic soda lye and settling, 93 per cent. of refined oil being thus obtained. A published analysis of Sea Island cotton-seed oil shows that it consists of glycerides of the following acids: myristic, 0.3; palmitic, 20; stearic, 2; arachidic, 0.6; oleic, 36.2; and linolic, 41.7 per cent. Upon chilling, it deposits so-called "cotton-stearine," composed chiefly of stearine mixed with some other glycerides, and when the stearine has been removed the oil is known as "winter oil," as it does not readily solidify in cold weather. The pressed cake is used as cattle food. The bleaching of cotton-seed oil is effected by means of fuller's earth. Most of the protein content of the cotton-seed meal when purified can be extracted at room temperature by a 10 per cent. solution of sodium chloride. Next to olive oil, the refined

American cotton-seed oil is the largest item in edible vegetable oils. The raw cotton contains about 1 per cent. of wax, which can be extracted after crushing by means of benzene. Cotton-seed oil if used alone produces soft soap. Cotton seeds, according to one report, yield 177 pounds of oil and 525 pounds of cattle feed per 1,100 pounds of seed.

*Reference: Cottonseed and Cottonseed Products*, by A. E. Bailey, Editor (Interscience Publishers, Inc., New York).

**COTTRELL PRECIPITATING PLANT (Lodge-Cottrell Process)** — An electrical arrangement for condensing mists and recovering valuable constituents of waste gases. It consists of two sets of electrodes, one connected with a source of high potential direct current and another to earth, the shape of the electrodes varying with the conditions of application. The suspended liquid or solid particles contained in the gases passing through the gap between the two electrodes become charged with electricity and are condensed, or deposited on the surface of the earthed electrode. This plant can be usefully applied for air-cleaning in workrooms; to cause the condensation of the mist-like fumes generated in the concentration of sulphuric acid; for the recovery of lead from the waste gases of lead furnaces; deposition of the suspended dust in the waste gases from cement works; deposition of arsenious oxide from the fumes yielded by roasting arsenical ores, and application to practically all kinds of fumes, including the collection of "tar fog" from the gases of gas-producers, coke-ovens, and distillation processes. The process can also be utilized for the fractional precipitation of mixed materials differing in volatility during operations conducted at different temperatures; for example, high-grade white arsenic can be separated from lead fume by the precipitation of lead and zinc compounds while the temperature is high enough to keep white arsenic in a gaseous state and the latter compound can be obtained by cooling the escaping gas. Smokes, fumes, and dusty gases may all be regarded as disperse systems, the dispersed substances being solid or liquid in a dispersion medium of gas.

Recovery efficiencies of 85 to 99 per cent. in the case of metallurgical fume and 99 per cent. in the deposition of pyrite burner dust by electrical means have been reported by P. E. Landolt, of the U.S.A. Research Corporation. (See Oliver Lodge (*J.S.C.I.*, 5, 572 (1886)); and "Design of Gas-Cleaning Installations" (*Ind. Eng. Chem.*, 29, 406 (1937).)

**COULOMB** — See Electricity.

**COULOMETER** — See Voltameter.

**COUMARIN** ( $C_6H_4 \cdot CH : CH \cdot COO$ ) — The aromatic principle of woodruff

(*Asperula odorata*), contained also in sweet-scented vernal grass and sweet clover (*Melilotus alba* and *officinales*), and in the Tonka bean (the fruit of *Dipterix odorata* in the form of small colourless crystals between the seed coating and the kernel), and being soluble in alcohol it can be easily extracted therefrom. There is reason for thinking it

results from the decomposition of a glucoside. In pure state it is colourless, crystalline, of m.p.  $70^{\circ}\text{C}.$ , readily soluble in alcohol, ether, and hot water, has an agreeable aromatic odour, while its vapour is said to act very strongly on the brain. It can be prepared from guaiacol, also synthetically from salicylic aldehyde, and is used in perfumery, and for flavouring.

**COUMARONE** ( $\text{C}_6\text{H}_4\text{-CH:CHO}$ ) is a colourless liquid occurring in that fraction of crude benzol obtained by coal-tar distillation which comes over between  $165^{\circ}$  and  $175^{\circ}\text{C}.$  It boils at  $175^{\circ}\text{C}.$  and can be isolated as picrate. Coumarone is the lactone of 2-hydroxycinnamic acid, and is converted into salts of the latter when boiled with aqueous alkalis. (See Coumarone Resin, and Gums and Resins (Synthetic).)

**COUMARONE RESIN (Para-Coumarone, Cumaron Resin, Benzofurane Resin)**—A resinous body of varying melting-point, soluble in ether, petroleum, turpentine, acetone, and carbon disulphide. It is gummy to hard in character, and is suitable for replacing ester gums, or even kauri gum, and others in varnish making and rubber substitutes. It is made by treatment of the distillate fraction of coal-tar naphtha (between  $160^{\circ}$  and  $200^{\circ}\text{C}.$ ), containing indene and coumarone, with either strong sulphuric acid or aluminium chloride, or by simply heating under pressure and subsequent separation from the polymerizing agent, when it sets to a solid resinlike mass of sp. gr. 1.05 to 1.10. Among other applications it is used for polishing coffee beans. (See Gums and Resins.)

**COUNTER**—See Geiger-Müller Counter.

**COWRIE**—See Gums (Kauri).

**COW-TREE WAX**—See Waxes.

**CRACKING**—See Petroleum.

**CREAM**—See Milk.

**CREAM OF TARTAR (Potassium Bitartrate, Potassium Acid Tartrate, Potassium Hydrogen Tartrate)** ( $\text{KHC}_4\text{H}_4\text{O}_6$ )—See Argol, Potassium Bitartrate, and Tartar.

**CREATINE** ( $\text{NH}_2\text{C(=NH)N(CH}_3\text{)CH}_2\text{COOH}$ )—A substance found in the muscles of various animals, and known to play a part in muscular contraction. Schoenheimer, in 1939, showed that creatine is biologically synthesized from glycine and arginine, and that creatinine ( $\text{NH=C.NH.CO.CH}_2\text{.N(CH}_3\text{)}$ ) arises from creatine by dehydration.

The former is an invariable constituent of urine.

**CREOSOL** ( $\text{C}_6\text{H}_3(\text{CH}_3)(\text{OCH}_3)(\text{OH})(1,3,4)$ )—A phenol ether. (See Creosote.)

**CREOSOTE (Coal Tar)**—A dark-coloured, thick liquid by-product from coal-tar distillation, generally containing phenols (which can be removed by treatment with caustic soda); used as a wood preservative and for the preparation of disinfectant liquids. With respect to its separation from tar and pitch, see Coal, Coke, and Tar.

**CREOSOTE (Wood)** — A colourless or faintly yellow liquid obtained from the distillation of wood-tar and consisting of a mixture of guaiacol, creosol, and other phenols. For medicinal purposes, it is preferably prepared from the twigs of *Fagus sylvatica* or *F. ferruginea* (Beechwood Creosote). It is soluble in alcohol and ether, and is slightly soluble in water; sp. gr. 1.080; b.p. between 200° and 230° C. It has a pungent, penetrating odour and a burning taste and is used in medicine for its antiseptic properties. (See Guaiacol, and Wood.)

**CREOSOTE CARBONATE** — A clear, colourless, or amber-coloured, viscid liquid consisting of the carbonic esters of the various constituents of creosote, prepared by passing a stream of carbonyl chloride (phosgene gas) into a solution of creosote in sodium hydroxide solution. The oily liquid which separates is first washed with a weak alkali solution and then with water. It contains an equivalent of about 90 per cent. of creosote, and was formerly used in medicine for the treatment of pulmonary tuberculosis and as an intestinal antiseptic. Sp. gr. 1.150 to 1.180.

**CRESOL** ( $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$ ), obtained from coal tar and present in the tar from pine and beech wood, is a homologue of phenol ( $\text{C}_6\text{H}_5\text{OH}$ ). There are three isomeric forms—ortho-, meta-, and para-cresol. Ortho-cresol is a crystalline intermediate which has a sp. gr. of 1.048°, b.p. 191° C., and m.p. 30.8° C.; meta-cresol is a liquid of sp. gr. 1.034, and b.p. 203° C., used in the manufacture of synthetic perfumes; para-cresol is a white crystalline intermediate of sp. gr. about 1.03, m.p. 35° C., and b.p. 202° C. Crude liquid cresol as obtained from the distillation of tar can be rendered soluble in or miscible with water by the use of resin or oil-soap and alkali, and in this form it constitutes the basis of many disinfectant preparations, sheep dips, and insecticides. Of the cresols (all of which exhibit strong germicidal properties), *meta-cresol* is the most powerful, and this is used in making synthetic resins and as a photographic developer. Useful application has been made industrially in respect of the capability of cresol for absorbing many vapours by solvent action, as, for example, those of ether-alcohol.

**CRESYLIC ACID** — An old name for cresol, but now used only for the crude mixture of cresols and phenols obtained from coal-tar and marketed as 97–99 per cent. cresols. Being phenolic in character, it forms water-soluble derivatives with alkali metal hydroxides, and is used in large quantities in the flotation treatment of ores.

**“CREX”** — A proprietary laundry detergent, stated to be free of silicate, caustic soda, and bleach.

**CRISTOBALITE** — See Silica.

**CRITH** — The weight of a litre of hydrogen at standard temperature (0° C.) and pressure (760 mm.)—viz., 0.08988 gram.

**CRITICAL DENSITY** — See Critical Points, and Densities.

**CRITICAL MASS** — The *minimum* amount of a fissionable material, such as uranium 235 or plutonium 239, that is required for a spontaneous chain reaction.

**CRITICAL POINTS**—The critical point is that at which two phases continually approximating each other become identical, forming one phase. Thus at a higher temperature the vapour generated from a liquid becomes a gas. The critical temperature is the highest temperature at which a given gas can be liquefied no matter what pressure is applied. *At this temperature* the corresponding pressure, density, and volume are observed. The critical temperature of water is  $374.0^{\circ}\text{C}.$ , the critical pressure  $217.72\text{ atm.}$ , critical density  $0.4\text{ gm. per c.c.}$ , and critical volume  $2.5\text{ c.c. per gm.}$ ; for carbon dioxide the corresponding values are  $31.1^{\circ}\text{C.}$ ,  $73.0\text{ atm.}$ , and  $0.46\text{ gm. per c.c.}$ , and  $2.2\text{ c.c. per gm.}$ ; and for oxygen  $-118.8^{\circ}\text{C.}$ ,  $49.7\text{ atm.}$ ,  $0.43\text{ gm. per c.c.}$ , and  $2.3\text{ c.c. per gm.}$  (See Matter).

**CRITICAL PRESSURE**—See Critical Points, and Gases.

**CRITICAL TEMPERATURES**—See Critical Points, and Gases.

**CRITICAL VOLUME**—See Critical Points, and Volume.

**CROCIDOLITE**—See Asbestos.

**CROCOISITE (Crocoite)**—A native lead chromate ( $\text{PbO}, \text{CrO}_3$ ), of crystal system No. 5, and sp. gr. 6.0. (See Lead, and Chromium.)

**CROCUS**—“Crocus of antimony” is the oxysulphide of that metal and “Crocus of Mars” is an old name for finely divided red oxide of iron. (See also Saffron.)

“**CRONITE**”—A heat-resisting alloy of the nickel-chromium class, the composition being given as approximately 65 per cent. nickel, 16 per cent. chromium, 1 per cent. manganese, 0.75 per cent. silicon, and 16 per cent. iron, withstanding a temperature of  $650^{\circ}$  to  $700^{\circ}\text{C}.$

**CROOKESITE**—A rare mineral containing copper selenide and about 17 per cent. thallium. (See Thallium.)

**CROTON OIL**—A fatty, yellowish-brown oil obtained by expression from the seeds of *Croton tiglium* (N.O., Euphorbiaceæ) which contain about 50 per cent. of the oil. It is soluble in alcohol and ether; sp. gr. 0.940 to 0.955. The active principle is a hard, pale yellow resinous substance named croton-resin and is a drastic purgative and skin vesicant. The plant is a native of India and the more easterly parts of Asia.

**CRUCIBLES**—Vessels or pots employed for heating solid chemical substances to a high temperature or for melting metals, etc. They are variously made of earthenware, plumbago, porcelain, silica, “Alundum,” platinum, iron, “Stellite,” silver, and nickel, but the metallic ones may not be employed for melting metals or under circumstances in which another metal may be reduced from the compound in use to its free (uncombined) state, on account of the danger of damaging or ruining the vessel through the production of an alloy by combination of the other metal with the metal of the crucible. Industrial crucibles are made of various refractory materials, such as fire-brick, and carbon. (See Refractories.)

**Gooch Crucible** — A cup of glazed porcelain, usually about  $1\frac{1}{2}$  inches high and of  $1\frac{1}{4}$  inches diameter at the top, tapering somewhat to the bottom, which is pierced with a number of small holes. A layer of asbestos is laid on this by pouring a suspension in water of the finely divided material into the cup, and allowing it to drain; then a perforated porcelain plate is laid on top of the asbestos "mat." The crucible is fitted into the neck of a vacuum flask, in which low pressure is maintained by a filter-pump. This arrangement serves for the filtration of solutions which would pass only very slowly through an ordinary paper filter or would act on it chemically. The crucible with the precipitate can be dried and ignited for weighing.

**"Alundum" Filtering Crucible** — Similar in use to Gooch crucible, but employing "Alundum" particles of controlled size bonded into the shape of a crucible.

**Fritted Glass Filtering Crucible** — Similar in use to Gooch crucible, but employing powdered glass particles of controlled size heated to the sintering point and moulded into disks, which are fused as bottoms directly to the wall of glass.

**CRUSHING AND GRINDING** — The mechanical size reduction of solid materials. Technically, crushing is the reduction of large lumps to relatively coarse particles; grinding further reduces these to a powder. It is inconvenient that there is no commonly accepted word for size reduction in general. "Comminution" might do, but it is not much used.

Mechanical size reduction is effected by applying enough force to the particles being treated to fracture them. The force may be applied in four principal ways: as pressure, shear, impact, or tearing. All crushing and grinding machines are devices for subjecting material to one or other of these forces, or, more usually, to a combination of them.

The kind of action most effective in comminuting a given material depends upon its physical properties, and especially on whether it is hard or soft, brittle or tough, free-flowing or sticky. Sticky materials are particularly difficult to handle. Where the stickiness is due to moisture it can be removed either by drying, or by adding more water to form a slurry. Thermoplastic materials such as pitch, which become sticky on heating, must be kept cool during treatment, say by air circulation through the mill.

As a very rough guide it may be said that brittle materials are generally best subjected to pressure or impact, and tough materials to shear or tearing. The hardness determines the amount of force which must be applied to each particle, and the materials of which wearing parts must be constructed to resist abrasion.

Crushing machines which operate chiefly by pressure include jaw crushers, gyratory crushers, and rolls, both plain and grooved. If the two elements of a pair of rolls are run at different speeds, as is often done, there is both pressure and shear. A common form of grinding machine which depends largely on pressure is the centrifugal roller mill, in which the material is distributed over the inside of a cylindrical

trough and ground under rollers held against the trough by centrifugal force.

Crushers which operate largely by shear include cone crushers of the coffee-mill type and disc mills of various kinds. The latter can also perform fairly fine grinding. A grinding device applying both shear and pressure is the edge runner or Chilean mill, often used for wet grinding.

Impact crushers include stamps, hammer mills, and cage mills. The two last also exert a tearing action, and hence are used for tough, fibrous materials such as tan bark. The high-speed hammer mill can also serve as a fine grinder. Other impact grinding machines include ball and tube mills, horizontal rotating cylinders filled with steel balls, flints, or other grinding media, through which the material to be ground is passed. The speed of rotation is such that the balls or flints are constantly carried up on one side and showered down upon the charge, pulverizing it by impact.

The above are a few of the great variety of crushing and grinding machines available. One other interesting device is the "Microniser," which has no moving parts. In this mill the material is subjected to intense turbulence by means of air or steam jets, whereby the particles are reduced by attrition to micron size.

With materials whose particles tend to agglomerate, the addition of traces of oleic acid, rosin, or other organic "grinding aids" markedly increases the grinding rate by preventing agglomeration.

The design of crushing and grinding machinery is still largely a matter of experience. Theoretical relations apply only very roughly. In general, the energy  $E$  required to pulverize a given weight of material conforms approximately to the relation:  $dE/dL = C/L^n$ , where  $L$  = diameter of particle,  $C$  = an empirical constant. For pure

pressure  $n=1$ , and the integrated expression is:  $E = C \log_e \frac{L_1}{L_2}$  where

$L_1$  and  $L_2$  are the initial and final particle diameters. This is known as Kick's Law. For pure shear  $n=2$ , and integration gives:

$E = C \left( \frac{1}{L_2} - \frac{1}{L_1} \right)$ , a relation known as Rittinger's Law. In practice  $n$  is

often between 1 and 2, and  $C$  varies widely for different types and sizes of machine.

*References:* Standard Chemical Engineering Works. (See Chemical Engineering.)

**CRYOHYDRATES** — See Solution.

**CRYOLITE** ( $\text{Na}_3\text{AlF}_6$ ) — A mineral double fluoride of sodium and aluminium, of crystal system No. 5, and sp. gr. 3.0, occurring abundantly on the coast of West Greenland; used as a flux and in enamelling; also in the glass industry and for glazing pottery. (See Aluminium, and Fluorine.)

**CRYOSCOPY** — Cryoscopy is the study of and determination of freezing points of liquids and solutions. It is generally associated with the effects of solutes in lowering the freezing point of solvents.

When a non-volatile solute is dissolved in a solvent the vapour pressure of the solvent is lowered as is indicated in the accompanying diagram.

When the solution curve meets the solid curve at  $T$ , it is at a temperature less than  $T_0$  (the freezing point of the solvent) and its vapour pressure is  $P_s$  which is less than  $P_0$  (the vapour pressure of pure liquid solvent and its solid phase). Thus we can say that the presence of the solute has changed the freezing point of the solvent,  $\Delta T_f = T_0 - T$ , by lowering the vapour pressure of the solvent. It is apparent from

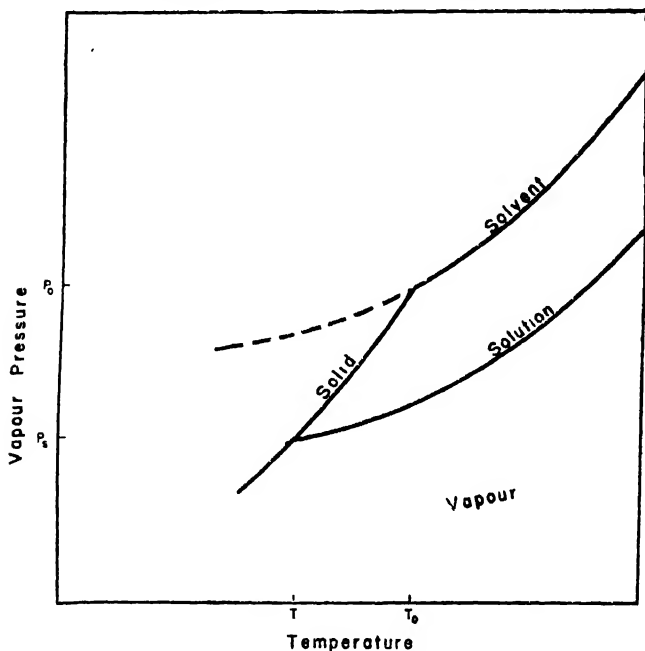


Diagram showing Vapour pressure-Temperature Curves of a Solvent and its Solution.

Raoult's Law that the amount of the lowering of the vapour pressure by a non-volatile solute will be proportional to the concentration of the solute, thus  $P_0 - P = P_0 N_s$  ( $P$ =vapour pressure of solution,  $P_0$ =vapour pressure of solvent,  $N_s$ =mole fraction of solute in solution).

In other words, the more concentrated the solution the lower its freezing point, that is to say, the vapour pressure curve of the solution would intersect the solid curve at a lower temperature. Therefore,  $\Delta T_f \approx N_s$ , or if we introduce a proportionality constant  $k_f$  which is characteristic of the liquid, then  $\Delta T_f = k_f N_s$ . For a dilute two-com-

ponent solution  $N_s = \frac{W_1}{W_2} \cdot \frac{M_2}{M_1} \times \frac{M_2}{M_2}$  where  $W_1$  and  $M_1$ =weight and

molecular weight of solute, while  $W_2$  and  $M_2$  = weight and molecular weight of solvent. In this case  $\Delta T_f = k_f \frac{W_1}{M_1} \times \frac{M_2}{W_2}$ . When concentration

is expressed in terms of molal concentration then  $\Delta T_f = K_f m$ , where  $K_f$  = molal freezing point constant for the solvent and  $m$  = molality of the solution.

Several types of apparatus for measuring freezing point depressions are available. The Beckmann apparatus and modifications are used with success. The modified equilibrium method as proposed by L. N. Adams, where a thermocouple is used to measure the temperature difference between the freezing solvent and solution, gives highly reliable results.

**CRYSTALLOIDS** — See Crystals.

**CRYSTAL CHEMISTRY** — Deals with the laws governing the arrangement of atoms in solids, and with the influence of the arrangement and electronic structure of atoms upon the physical and chemical behaviour of solids. (See Crystals, and Physics of Metals.)

**CRYSTALS AND CRYSTALLIZATION** — Substances of definite symmetrical or geometrical form—the reverse of the amorphous state. If some common alum be dissolved in cold water until it will dissolve no more, or, in other words, until the solution is saturated at the observed temperature, and then transferred to an evaporating dish and more alum dissolved by the aid of heat until again the solution is saturated at this higher temperature, it will, upon cooling, deposit a mass of crystallized alum, that further quantity which was dissolved by the aid of applied heat.

Some liquids exhibit a suspension or retardation of crystallization or solidification, for example, glycerine may be cooled to  $-30^\circ\text{C}$ . without solidifying, but upon the addition of a crystal of the solid substance, the whole quantity freezes at once, and will not melt again until a temperature of  $15.5^\circ\text{C}$ . is reached. This phenomenon is known as **super-cooling**, and is exhibited by most solutions and liquids, including water. The normal temperature at which water freezes is, according to Robert Smith-Johannsen (*Science*, **108**, 652 (Dec. 10, 1948)), in the absence of any known foreign nucleating materials, very close to  $-20^\circ\text{C}$ . Four sets of experiments showed values between  $-18.0^\circ\text{C}$ . and  $-20.0^\circ\text{C}$ . Furthermore, the crystallization temperature was found to be independent of the rate of cooling, of the previous history such as previous freezing, and of the temperature to which the water was raised between freezing cycles.

Crystallization is often resorted to as a means of purifying a particular constituent of a solution from accompanying and less crystalline substances or bodies devoid of crystalline form, although it has been established as a fact that practically all crystals contain inclusions of mother-liquor extremely difficult to remove. Agitated crystallization is used when great purity is desired, as the smaller the crystals the greater the purity. A substance in solution in less concentration than

that corresponding to saturation at a given temperature remains in the solution or mother-liquor.

Many chemical salts have the property of combining with water in assuming the crystalline form from a state of solution; thus cupric sulphate, which has the formula  $\text{CuSO}_4$  in its anhydrous form, crystallizes from water in chemical combination with 5 molecules of water ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), magnesium sulphate with 7 molecules ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), and so on, and water so combined is termed **water of crystallization**. In some cases crystals lose water *in vacuo*, and the water of crystallization is generally expelled from salts by heating to  $100^\circ \text{C}$ . (See Efflorescence.)

Pope has defined a crystal as an arrangement of matter in which every point is repeated with a similar environment throughout the structure, and has directed attention to the fact that certain doubly-refracting liquids retain some element of the homogeneity of crystal structure possessed by the crystalline solids from which they are produced, as, for example, ethyl *p*-azobenzoate.

To use the words of U. R. Evans, "the essential character of a crystal is an *ordered* internal arrangement of the component atoms on a definite lattice," and all modern studies of the crystal nature start from this idea.

Crystals may be **classified** as follows:

(1) The *cubic* isometric or regular system, having three equal and interchangeable axes at right angles, comprising five crystal classes, including, for example, rock salt, alum, diamond, pyrite, galenite, fluor spar, and most metals.

(2) The quadratic, square prismatic, or *tetragonal* system, having three axes, all at right angles, two of which are equal and interchangeable, comprising seven classes, of which potassium dihydrogen phosphate, potassium ferrocyanide, tinstone, zircon, and nickel sulphate are examples.

(3) The *hexagonal* system, having four axes, three of which are equal and interchangeable (therefore, at an angle of  $60^\circ$  to each other) and all three at right angles to the fourth axis, comprises five subdivisions, and in these quartz, lead iodide, apatite, "Carborundum," and snow are included.

(4) The *rhombohedral* or trigonal system, having axes as for the hexagonal system, but one axis of symmetry at  $120^\circ$  intervals (whereas the hexagonal system has one axis of symmetry at  $60^\circ$  intervals), comprising seven subdivisions, including calc spar, olivenite, mispickel, celestine, corundum, hæmatite, and graphite.

(5) The *rhombic*, orthorhombic or prismatic system, having three unequal axes, all at right angles, comprising three groups, as exemplified by magnesium sulphate, potassium sulphate, nitre, potassium permanganate, potassium chlorate, and sulphur.

(6) The *monoclinic* or monosymmetric system, having three axes, all unequal, two of which are at right angles, comprising three subdivisions, including gypsum, borax, soda crystals, tartaric acid, sucrose, and feldspar.

(7) The *triclinic*, asymmetric, or anorthic system, having three axes, all unequal and inclined, comprising two divisions, of which copper sulphate, potassium dichromate, potassium ferricyanide, and boric acid, are illustrative.

Many chemical bodies assume the crystalline state when they change from the liquid or gaseous condition into the solid form ; upon cooling of fused masses such as sulphur and antimony, or upon sublimation, as, *e.g.*, iodine, phosphorus, and arsenious oxide.

The diamond and many other precious stones probably result from processes of fusion effected under great pressure, and a very large number of definite chemical bodies are found in nature in a crystalline condition.

Crystalline bodies are really the simplest kind of solids, the molecules being locked together in regular structure.

Definitely crystalline bodies exhibit a peculiar susceptibility to cleavage, that is, being split in some directions more readily than in others, and of allowing heat and light rays to pass more readily in certain directions as compared with others, thus giving rise to the phenomena of double refraction. Crystals of class 1, since the internal arrangement is a uniform one, are exceptions in the matter of behaviour when subjected to heat, light, etc. Physicists regard the spectra furnished by crystals, when subjected to X-rays, as furnishing information concerning the arrangement of the atoms in the crystal, and concerning the number of molecules associated with the crystal unit cell. It depends upon the measurements of the angles of incidence of X-rays which show maxima and minima of interference in the reflected rays. According to W. H. Bragg and W. L. Bragg, the atoms in a crystal are independent of each other, being arranged in a regular order at measurable distances between. (See *Concerning the Nature of Things*, by W. H. Bragg, an excellent popular account of this and related fields.) In certain cases, such as that of potassium chloride, every "atom" (ion) occupies a symmetrical position in the crystal structure, each potassium ion being symmetrically surrounded by six chloride ions, and each chloride ion by six potassium ions in a space lattice. In the diamond, every carbon atom is symmetrically surrounded by four other carbon atoms, arranged at the corners of a tetrahedron in such manner that the whole crystal is one continuous molecule, thus explaining, as is thought, its great density and hardness.

It would also appear that the internal molecular structure of crystals is such that the maximum electrostatic stability is attained.

Concerning the magnetic properties of crystals, it is known that their diamagnetic susceptibilities vary with direction in the crystals, and it has been ascertained that the variations are related to the arrangement of their ionic or molecular groups in the lattices.

Little or nothing is yet known of the determining *causes* of the formation of crystals or why various substances assume varying crystalline forms. Alum, for instance, sometimes crystallizes in cubes and at other times in octahedra, and similarly common salt, which ordinarily crystallizes in cubes, assumes the octahedral form when a small quantity of urea is present in the solution.

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The size of crystals is dependent on the molecular concentration and on the degree of supersaturation taken in conjunction therewith. As a rule they are of larger size when solutions of salts are not too concentrated and are allowed to cool slowly. In manufacturing crystallization operations, among other difficulties encountered is that of latent heat, which is generally of the order of 100 B.Th.U. per lb. of crystals produced.

Factors influencing the formation of crystals from an unseeded solution are (1) rate of cooling, (2) intensity of agitation, (3) purity of the solution, (4) temperature, (5) concentration, and (6) presence of dust. Solutions composed of different materials vary enormously in their tendencies to form crystal nuclei.

Substances capable of assuming crystalline form are classified as *crystalloids* to distinguish them from *colloids*—that is, substances which cannot be definitely crystallized—and from the larger class of so-called *amorphous* substance.

**Isomorphous** substances are those which crystallize in the same form, such as the sulphates of zinc and magnesium, whereas when a substance (such as sulphur) is capable of crystallizing in two forms it is termed **dimorphous**. Isomorphous analogous chemical substances can replace each other wholly or partially in many crystalline compounds without alteration of the crystalline form. The view is generally held that when two substances have forms identical in crystallographic system, the molecules contain an identical number of atoms similarly united.

*References:* "Crystal Structure and Chemical Constitution" (a general discussion, Faraday Society, 1929); "The Study of Crystals, with Special Reference to Chemistry," by A. Stuart (*Chem. and Ind.*, **49**, 989 (1930)); *An Introduction to Crystal Analysis*, by W. Bragg (G. Bell and Sons, London); *The Structure of Crystals*, by Wyckoff (Reinhold Publishing Corp., New York); *X-Rays and Crystal Structure*, by W. H. and W. L. Bragg (G. Bell, London); *Crystal Chemistry*, by C. W. Stillwell (McGraw-Hill Book Co., New York); *A Study of Crystal Structure and Its Applications*, by W. P. Davey (McGraw-Hill Book Co., New York); *The Chemistry of Solids*, by C. H. Desch (Cornell Univ. Press, Ithaca, New York); *Crystals and X-Rays*, by K. Lonsdale (D. Van Nostrand Co., New York); *Crystal Structures*, by R. W. G. Wyckoff (Interscience Publishers, New York); *Applied X-Rays*, by G. L. Clark (McGraw-Hill Book Co., New York); *Crystal Growth*, by H. E. Buckley (John Wiley and Sons, New York); *Annual Reports of the Progress of Chemistry* (Chemical Society), section on Crystallography, especially 1946, p. 62; Amorphous, Colloidal State, Dialysis, Matter, and Silicon (Dioxide).

**CRYSTAL VIOLET (Gentian Violet, Methylrosaniline)**—A rosaniline dye (Colour Index No. 681), being the hydrochloride of hexamethyl-*p*-rosaniline, and occurring in the form of greenish crystals having a metallic lustre and dissolving in water to give an intensely violet solution. It is used in medicine externally for the treatment of staphylococcal infections and internally for threadworms.

"C.T.A.B." — See Cetrimide.

**CUBA WOOD** — See Fustic.

**CUBEBS, OIL OF** — A colourless or pale green volatile oil obtained by steam distillation from the fruit of *Piper Cubeba*, indigenous to Java and cultivated in Sumatra and Borneo. It contains a crystalline sesquiterpene alcohol known as cubeb camphor ( $C_{15}H_{25}OH$ ) together with dipentene, *l*-pinene, camphene and cadinene; soluble in alcohol and ether; sp. gr. 0.910 to 0.930 at 15° C.; ref. ind. 1.485 to 1.500 at 20° C.; opt. rot. -20° to -35° at 20° C.

**CUBIC CENTIMETRE (c.c.)** — Based upon the definition that 1 kilogram of water at 4° C. occupies a volume of 1 litre, the Joint Committee for the Standardization of Scientific Glassware advises the use of this unit and its sub-divisions (1 l., 10 dl., 100 cl., 1,000 ml.) in the scientific measurement of liquid volumes. This unit differs slightly—but only slightly—from that previously used, namely, 1 cubic decimetre or 1,000 cubic centimetres. The exact equivalence is: 1 litre equals 1,000.027 cubic centimetres. (See Weights and Measures.)

**CUCUMBER OIL (Gourd Oil)** — A greenish-yellow drying oil expressed from cucumber and pumpkin seeds (genus *Cucurbitaceæ*), soluble in alcohol, ether, etc.; sp. gr. 0.923, cap. v. 188.7, and i.v. 121; used as fuel, for illuminating, and in medicine.

**CUDBEAR** — See Archil.

**CUICUS BENEDICTUS OIL** — From the seeds of *Cuicus benedictus*; sp. gr. at 15° C. 0.9255, sap. v. 196.5, acid. v. 16.6, i.v. 139.6. It is a semi-drying oil similar to hemp oil, and suitable for making soap and varnish.

**CULLET** — See Glass.

**CULM** — Coal dust, especially that of anthracite.

**CUMARON RESIN** — See Coumarone Resin, and Gums and Resins.

**CUMARÚ OIL** — See Tonka-Beans.

**CUMENE** ( $C_6H_5.CH(CH_3)_2$ ) — A liquid homologue of benzene, of sp. gr. 0.864, and b.p. 153° C.; soluble in alcohol and ether, and yields benzoic acid on oxidation. (See Petroleum (Special Fuels).)

**CUMIN ALDEHYDE** — See Perfumery.

**CUMMIN OIL** — A colourless or pale yellow volatile oil distilled from the fruit of Roman caraway, *Cuminum Cyminum*, indigenous to Egypt and cultivated in Arabia, India, and China. It contains about 35 per cent. of cuminic (cumin) aldehyde together with some cumene and pinene; sp. gr. 0.910 to 0.935 at 15° C.; ref. ind. 1.495 to 1.509 at 20° C.; opt. rot. +3° to +8° at 20° C.

**CUPELLATION** — An operation conducted in a *cupel* (*cupola*), that is, a shallow, oval-shaped bone-earth or other dish which is heated in a reverberatory furnace in course of assaying, testing, or refining metals. (See Silver.)

**CUPFERRON** ( $C_6H_5(N.NO)O.NH_4$ ) — The ammonium salt of nitroso-phenylhydroxylamine. It is a colourless crystalline body soluble in water, used in the practice of quantitative analysis for the determination of uranium; also for separating copper and iron from other associated metals (they alone being precipitated by cupferron from strongly acid solutions). The precipitate is washed on a filter first with water and then with ammonium hydrate, which dissolves the copper but not the ferric compound, which is soluble in chloroform, ether, and acetone, and may thus be obtained free from other associated metallic salts. The ferric compound can be converted into oxide by ignition and weighed as such. The use of this reagent is limited by reason of its explosive character.

“**CUPRADOR**” — A corrosion-resisting, copper-bearing steel.

**CUPRAMMONIUM SILK** — See Silk Substitutes.

“**CUPREN**” — The name given to certain acetylene polymerization products containing only 0.2 to 0.3 per cent. copper, obtained by the action of copper oxide on acetylene at about 230° to 260° C. They are high-molecular, quite insoluble bodies, used in compounding certain explosives, stated to be superior to dynamite; for example, eleven parts by weight of nitroglycerine mixed with one part by weight of the polymerized acetylene. “Cupren” is also stated to be useful in compounding liquid oxygen explosives.

**CUPRITE** — See Copper.

**CURARE** (*Curara*, *Curari*) — A dark brown, resinous extract varying in consistency from a thick syrup to a dark brown amorphous solid, prepared and used in the remote valleys of the Amazon and Orinoco by the South American Indians to poison their arrows. Its preparation has been a closely guarded secret and the botanical source of the drug is not conclusively known. Three types of the drug have been described according to the container in which they are packed; Pot Curare is packed in small clay pots, Calabash Curare occurs packed in small calabashes about the size of a large pear, and Tube Curare is packed in bamboo tubes. Formerly, the botanical source of all curare was ascribed to *Strychnos toxifera* and other species of *Strychnos*, but it now seems most probable that the Tube variety is derived from *Chondrodendron tomentosum*. Of the forty different alkaloids obtained from the various types of curare, *d*-tubocurarine ( $C_{38}H_{44}O_6N_2$ ) which has been isolated from Tube Curare and obtained in a crystalline form as the chloride, has been found to be the most active in producing muscular relaxation whilst being less toxic than the other alkaloids. It is now used in medicine to produce muscular relaxation during abdominal and other surgical operations and to prevent convulsions during the electrical treatment of mental patients. Its action in paralysing the skeletal muscle is effected by blocking the nerve impulse at the myoneurial junction and is thought to result from the neutralization of the acetylcholine reaction. (See *Curare, Its History, Nature and Clinical Cases*, by A. R. McIntyre (University of Chicago Press); Marsh *et al.*,

on the curariform activity of chondrodendrine and *iso*-chondrodendrine derivatives in *J. Pharmacol.*, **92**, 454 (1948); **93**, 109 (1948); W. D. M. Paton's review of the pharmacology in *J. Pharm. et Pharmacol.*, **5**, 273 (1949); and *d*-Tubocurarine.)

**CURCAS OIL** — Yielded to extent of from 32 to 33 per cent. from the seeds of *Jatropha curcus* (Linn.), or "physic nut" of the East Indies. It exhibits purgative, emetic, and drying properties; sp. gr. 15°/15° C. 0.9191, sap. v. 191.6, and i.v. 98.7. The plant which is commonly found as a hedge growth in Siam is of similar character.

**CURCUMENES** — Terpenes contained in the essential oil obtained from the rhizomes of *Curcuma aromatica*, Salise.

**CURCUMIN** — See Turmeric.

**CURIE** — The amount of activity of radon in equilibrium with 1 gram of radium. The standard measure of the rate of radioactive decay, equal to  $3.71 \times 10^{10}$  disintegrations per second.

**CURITE** — A radioactive crystalline mineral found at Kasolo (Belgian Congo), giving upon analysis the composition  $\text{PbO}_5, \text{UO}_3, 4\text{H}_2\text{O}$ .

**CURIUM** (Cm) — Element number 96, discovered by G. T. Seaborg, R. A. James, and L. O. Morgan in 1944, and accepted (1949) by the International Union of Chemistry. Curium was made by the bombardment of plutonium with alpha particles in a cyclotron.

**CURUÁ OIL** — Obtained from the kernel of a Brazilian palm tree. The kernels yield 60 per cent. of oil, which is used for edible purposes and for soap making.

**CUSCUS OIL** — See Vetiver Oil.

**CUTCH** — See Catechu, and Tannins.

**CUTTING FLUIDS** are lubricating agents for use with machine cutting-tools, one function of which is to keep the working parts cool, and, apart from its rusting action, water is a suitable agent. To avoid rusting, soda or soap are often used in association, whilst lard oil is recognized as nearly indispensable in certain cutting operations, and certainly superior to mineral oils, having a much higher adhesion for metal. Other oils, such as sperm, castor, and rape, partake of the advantages exhibited by lard oil, and triethanolamine is advocated as a base for cutting oils in the form of the oleate soap. Emulsions of various animal, vegetable, fish, and mineral oils are often employed, and are said to be suitable for drilling, reaming, milling, planing, and sawing. For tapping and threading, lard oil and others resembling it are recommended, but the character of the operation and the nature of the metal determine the choice of the cutting liquid. (See Lubricants.)

**CUTTLE-FISH** — A molluscos animal of the order *Cephalopoda* and genus *sepia*, possessing a so-called "ink bag"—a gland near the liver—from which it discharges, when pursued, a dark-coloured liquid which discolours the water and obscures its passage. It is from this material that the *sepia* of painters is prepared, by dissolving it in potassium K.C.E.—10

or sodium hydroxide, reprecipitation with hydrochloric or sulphuric acid, washing and drying. Sepia is dark brown in colour, of fine grain, and is stated to consist of a mixture of calcium and magnesium carbonates, melanin, and an organic colouring matter. Cuttle-fish bone is composed of calcium carbonate 89.30 per cent., insoluble mineral matter 0.23 per cent., organic matter 9.44 per cent. containing 0.72 per cent. nitrogen, iron oxide and alumina 0.33 per cent., phosphoric acid traces, and undetermined matter 0.70 per cent. It makes a good poultry grit and liming material for soils, and is also used in making tooth powder and polishing powders. The cuttle-fish, allied to *Elodone moschata*, is said to contain the odorous principle of ambergris, and these cephalopods are consumed by the sperm whale. (See Ambergris.)

**CYANAMIDE** ( $\text{CN}_2\text{H}_2$  or  $\text{H}_2\text{N.CN}$ ), when pure, is a colourless, crystalline body, prepared from cyanogen chloride and an ethereal solution of ammonia. It is deliquescent, melts at  $40^\circ\text{C}$ ., is soluble in water, alcohol, and ether, and behaves chemically both as a weak base (forming crystalline salts with acids) and as a weak acid (yielding sodium, lead, silver, and calcium compounds). It exhibits some toxic action, persons working with it being liable to fleeting exanthemata of the head and chest, etc.

Calcium cyanamide is commercially produced by heating calcium carbide in the presence of a little calcium chloride to about  $1,000^\circ\text{C}$ . in a current of air or nitrogen, the heat being produced by an electric current passing through carbon resistances placed in the powdered carbide ( $\text{CaC}_2 + \text{N}_2 = \text{CaCN}_2 + \text{C} + 74,990$  calories) or by passing nitrogen (obtained from liquefied air) over a mixture of lime and carbon electrically heated to  $2,000^\circ\text{C}$ ., an excess of carbon being used. The crude product is a black powder containing 58 to 60 per cent. of calcium cyanamide, and is used as a fertilizing agent under the name of "nitro-lime," the nitrogen content being transformed by chemical changes into ammonia when the substance comes into contact with water. It does not suffer loss of nitrogen on storage. The other constituents of nitro-lime are about 20 to 22 per cent. of free lime, 8 to 9 per cent. of silica, alumina, and iron, and 11 to 12 per cent. of carbon in the form of graphite. Calcium cyanamide does not, it is stated, appeal to farmers very much as a fertilizer, and possibly this is because under certain soil conditions it polymerizes to calcium dicyanodiamide. In any case, it has to undergo changes which result in the production of ammonia for it to become effective. As a result of field trials, E. J. Russell has shown that in comparison with nitric nitrogen with an effectiveness of 100, ammoniacal nitrogen shows 97 and cyanamide 90 or less.

When it is desired to utilize cyanamide to produce ammonia, ground up fine, after first of all being damped to get rid of any unchanged carbide, and then heated in an autoclave with superheated steam at 150 pounds pressure, when the change represented as follows occurs:  $\text{CaCN}_2 + 3\text{H}_2\text{O} = \text{CaCO}_3 + 2\text{NH}_3$ ; the ammonia thus liberated is utilized as described under Nitrogen.

Nitrogen is also passed over a mixture of barium carbonate and carbon at high temperatures, when barium cyanide is formed, a carbide being first of all produced; this takes up nitrogen and yields a mixture of cyanide and cyanamide, which last-named compound, combining with a further amount of carbon, forms cyanide. (See Wæser's *The Atmospheric Nitrogen Industry*, vol. ii. (J. and A. Churchill, London); and H. A. Curtis' *Fixed Nitrogen* (Reinhold Publishing Corp., New York).)

**CYANAMIDE HYDROCHLORIDE** ( $\text{CN}_2\text{H}_2 \cdot 2\text{HCl}$ ) is a colourless crystalline salt of fairly stable character, which decomposes readily at  $100^\circ\text{C}$ ., and is far less hygroscopic than cyanamide.

**CYANIC ACID** — See Cyanogen Compounds.

**CYANIDATION** — See Ores.

**CYANIDES** — See Hydrocyanic Acid, Cyanamide, and Cyanogen.

**CYANITE (Kyanite)** — A mineral allied to *andalusite* and *sillimanite* ( $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ), but of different crystalline forms, occurring in varying colours—red, yellow, and blue. The Indian variety is stated to be entirely converted into *mullite* crystals and a siliceous glass upon firing to  $1,450^\circ\text{C}$ . (See Sillimanite.)

**CYANOGEN AND ITS COMPOUNDS**—Cyanogen ( $\text{C}_2\text{N}_2$ ) is a very poisonous, colourless gas, soluble in water and alcohol, having an odour something like that of bitter almonds, and which behaves in many respects as a halogen, the group CN playing the part of a radical. It is obtained by heating mercuric cyanide and collecting it over mercury (as it is soluble in water), and can be condensed to a colourless liquid of sp. gr. 0.87. According to B. Ricca, the gas can be best collected over a saturated solution of sodium sulphate or chloride acidulated with 10 c.c. hydrochloric acid per litre, the gas being practically insoluble in that medium. It is inflammable, and when burned is resolved into carbon dioxide and nitrogen. In combination with hydrogen it forms hydrocyanic acid (HCN).

Carbon and nitrogen do not combine directly, but when heated together with an alkali such as potassium carbonate, or by heating a mixture of potassium carbonate and carbon in a stream of ammonia gas, potassium cyanide (KCN) is formed. Potassium cyanide is also made by the fusion of calcium cyanamide with potassium hydroxide.

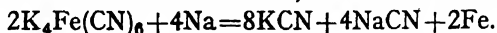
Sodium cyanide can be prepared by heating sodamide with charcoal, sodium cyanamide being thus produced, and subsequently resolved into the cyanide.

The process based upon the equation:  $\text{Na}_2\text{CO}_3 + 4\text{C} + \text{N}_2 = 2\text{NaCN} + 3\text{CO}$ , consists in heating a mixture of sodium carbonate and carbon in a stream of nitrogen or producer-gas under a pressure of 15 lbs. to the sq. inch in the presence of a suitable catalyst such as ferric oxide in admixture with an alkaline halide (sodium fluoride), the product being subsequently leached and otherwise dealt with so as to yield sodium cyanide of 96 and 98 per cent. purity.

Sodium cyanide can also be produced in good yield by heating at  $1,000^\circ\text{C}$ . in an electric furnace a mixture of sodium sulphate, barium

carbonate, and carbon, using iron powder as a catalyst, in a slow stream of nitrogen.

A mixture of alkaline cyanides is produced when potassium ferrocyanide is fused with metallic sodium, the reaction being as follows :



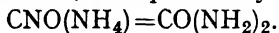
The fused fluid mass of cyanides can be poured off from the metallic iron, and forms a snow-white mass upon cooling.

The cyanides of the alkali and alkali-earth metals are all soluble in water, but those of the heavy metals, excepting mercury cyanide, are insoluble in water. The potassium and sodium cyanides are largely used in the extraction of gold and silver from their ores, also in electroplating and other industries.

Cyanogen compounds are made on an extensive scale from nitrogenous organic matters, such as the clippings of hoofs and hides ; thus, when heated with iron and potash, potassium ferrocyanide is produced.

**Cyanogen Chloride** (CNCl) is a colourless poisonous liquid of boiling-point  $13^\circ \text{C}$ ., soluble in alcohol, and used in making poison gases.

**Cyanic Acid** (HCNO) is a volatile mobile liquid of pungent odour like that of strong acetic acid, and unstable nature, changing with explosive violence into the polymeric bodies, cyanuric acid  $(HCNO)_3$  and cyanamide  $(HCNO)_x$ , when removed from a freezing mixture. By combination with bases it forms cyanates, including ammonium cyanate, which gradually undergoes change at ordinary temperatures, and at  $100^\circ \text{C}$ . is quickly resolved into urea, as expressed by the following :



This is a striking instance of isomeric change by atomic reconstruction brought about by a physical cause. (See Isomerism.)

**Hydrocyanic Acid** — See same.

**Hydroferricyanic Acid**  $(H_3Fe(CN)_6)$  crystallizes in brown needles, but is readily decomposable, while **hydroferrocyanic acid**  $(H_4Fe(CN)_6)$  crystallizes in the form of white needles, and both of them combine with a number of organic bases forming salts.

**Ferricyanides** are compound cyanides produced from ferrocyanides by the action of oxidizing agents, for example, potassium ferrocyanide  $(K_4Fe(CN)_6)$  becomes converted into potassium ferricyanide  $(K_3Fe(CN)_6)$  when dissolved in water and treated with chlorine.

**Ferrocyanides** are compound cyanides of iron and other metals, of which potassium ferrocyanide is typical. They are produced from ferricyanides by the action of reducing agents, potassium ferricyanide, for example, yielding the ferrocyanide by the action of grape sugar in presence of potassium hydroxide. A process of manufacturing sodium ferrocyanide, which has been carried out in Canada successfully, consists in first of all making sodium cyanide by fluxing a mixture of crude calcium cyanide, rock salt, and calcium carbide in an electric furnace and boiling the solution of the product with a ferrous salt, thus yielding a quantitative amount of sodium ferrocyanide. (See Carbonyl Ferrocyanides, Potassium Compounds (Prussiates), and Prussian Blue.)

**CYCLIC** — A term applied to compounds containing a ring of atoms in the nucleus. Carbocyclic (homocyclic) compounds are those in which the ring or closed chain is composed entirely of carbon atoms, such as the naphthenes and the benzene derivatives, including naphthalene and anthracene. Heterocyclic compounds are those in which the ring contains one or more other atoms than those of carbon, *e.g.*, pyridine ( $\text{CHCHCHCHCH}$ ), thiophene ( $\text{CH : CH.CH : CH}$ ), and furan

$$\begin{array}{c} | \quad \quad \quad | \quad \quad \quad | \\ \text{---N---} \quad \quad \quad \text{---S---} \quad \quad \quad \text{---O---} \\ | \quad \quad \quad | \quad \quad \quad | \end{array}$$

( $\text{CH : CH.CH : CH}$ ). (See Chains.)

**CYCLOBARBITONE** — A white, crystalline solid, namely, 5-ethyl-5- $\Delta^1$ -cyclohexenyl-barbituric acid; slightly soluble in water, soluble in alcohol and in solutions of alkaline hydroxides; m.p.  $173^\circ$  to  $176^\circ \text{C}$ . Used in medicine as a mild hypnotic.

**CYCLOHEXANE** ( $\text{C}_6\text{H}_{12}$ ) — Completely hydrogenated benzene, is a liquid of b.p.  $81^\circ \text{C}$ .; m.p.  $6.5^\circ \text{C}$ .; density 0.779. It distils without decomposition and is a good solvent—resembling paraffin more than  $\blacktriangle$  benzenoid hydrocarbons—for waxes and rubber.

**CYCLOHEXANOL** — See “Hexalin,” Hydrogenated Phenols, and Sex-tate.

**CYCLOHEXANONE** ( $\text{CH}_2(\text{CH}_2)_4\text{CO}$ ) — Produced by the oxidation of cyclohexanol. B.p.  $156^\circ \text{C}$ . and sp. gr. 0.947. On oxidation it yields adipic acid on account of which it is important in the preparation of nylon, and is recommended for addition (to the extent of 5 volume per cent.) to lubricating oil as a “penetrant” (penetrating the spaces between the moving parts of machines in a brief time, and also reducing friction between these parts).

**CYCLOHEXYLAMINE** ( $\text{C}_6\text{H}_{11}\text{NH}_2$ ) — A colourless liquid, sp. gr. 0.8647, b.p.  $134.5^\circ \text{C}$ ., crystallization point  $-17.7^\circ \text{C}$ ., ref. ind. at  $25^\circ \text{C}$ . 1.4565, flash point below  $0^\circ \text{C}$ ., miscible with water, alcohols, ethers, ketones, esters, aliphatic and aromatic hydrocarbons, and chlorinated hydrocarbons. Used as an insecticide, plasticizer, inhibitor of corrosion, accelerator for vulcanization of rubber, for cyclohexylamine soaps, for the absorption of acid gases, such as carbon dioxide, sulphur dioxide, and hydrogen sulphide, as an emulsifying agent with fatty acids, and as an intermediate for dyestuffs and allied chemicals.

“**CYCLONITE**” — See Explosives.

**CYCLOPROPANE** (Trimethylene) ( $\text{CH}_2.\text{CH}_2.\text{CH}_2$ ) — A colourless hydro-carbon gas, of pungent and slightly sweetish odour, b.p.  $-34^\circ \text{C}$ ., inflammable, supplied under pressure in steel containers, and used as a general anæsthetic. Cyclopropane is made by treating 1,3-dibromopropane with zinc and alcohol under controlled conditions. See “Cyclopropane: A New and Valuable Gas Anæsthetic,” by L. F. Sise, P. D. Woodbridge, and U. H. Eversole (*New England Journal of*

*Medicine*, Aug. 15, 1935); "Cyclopropane Anæsthesia: Postoperative Morbidity in 2,200 Cases," by E. R. Schmidt and R. M. Waters (*Anæsthesia and Analgesia*, Jan.-Feb., 1935); the chemistry of cyclopropane in Adriani's *The Chemistry of Anæsthesia*.

**CYCLOTRON** — An apparatus designed by Lawrence and Livingstone in 1931 to impart high energy to protons (hydrogen nuclei), deuterons (heavy-hydrogen nuclei), or alpha particles (helium nuclei). With applied voltages of the order of thousands the device produces energies of the order of millions of electron volts.

**CYBOPOGON OIL** — Distilled from *Cymbopogon clandestinus*, etc., in Burma; sp. gr. at 15°/15° C. 0.9319 to 0.9734, soluble in 70 per cent. alcohol at 15° C.; it is of pleasant odour, resembles ginger-grass oil, and contains carvone.

**CYMENE (Cymol)** ( $\text{CH}_3\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{CH}_3)_2$  (1, 4)) — A benzene hydrocarbon, found in the volatile "cummin oil" obtained from *Cuminum cyminum*, also in water-hemlock seeds and in oil of thyme. It is produced as a by-product in preparing cellulose from wood by the sulphite process. It is nearly related to camphor ( $\text{C}_{10}\text{H}_{16}\text{O}$ ) (from which it can be readily obtained by a process of dehydration) and to the terpenes ( $\text{C}_{10}\text{H}_{16}$ ), from which it can also be prepared. It boils at 176° C., has a sp. gr. of 0.857, is soluble in alcohol and ether, colourless, and has an agreeable camphoraceous and lemon-like odour. There are many isomeric cymenes, and it is stated that eighteen varieties have actually been prepared. Para-cymene is used in the synthetic making of menthol and thymol.

**CYSTEINE** — An important amino-acid ( $\text{HS}\cdot\text{CH}_2(\text{NH}_2)\cdot\text{COOH}$ ). See Cystine.)

**CYSTINE** — An amino-acid  $\left( \begin{array}{c} \text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{COOH} \\ | \\ \text{S}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{COOH} \end{array} \right)$  found in the

bodies of plants and animals and among the hydrolytic products of albumins containing sulphur, such as casein, and notable as a constituent of wool. It is important biologically as a hydrolytic product of sulphur-containing proteins, and along with cysteine as an essential oxidation-reduction mechanism in the body.

"**CYTAMEN**" — A proprietary name for a preparation containing vitamin  $\text{B}_{12}$  from biological sources. (See Vitamins.)

**CYTASE** — One of the enzymes in germinating barley which attacks and destroys the cell walls, thus exposing the starch content to the action of the diastase.

**DAIRY CHEMISTRY** — See Milk.

**DAKIN'S SOLUTION** — An antiseptic solution of sodium hypochlorite containing 0.50 to 0.55 per cent. available chlorine. Used for the irrigation of wounds. (See Eau de Javelle.)

**DALTON'S ATOMIC THEORY** — See Atoms.

**DALTON'S LAW** — See Gas Laws.

**DAMIANA** — The dried leaves of *Turnera diffusa* (South-west Texas and Mexico), containing an oil of volatile nature and odour like chamomile.

**DAMMAR (Black)** — See Gums and Resins.

**DAMMARA RESIN (Dammar Gum)** — See Gums and Resins.

**DANAITE** — A cobaltiferous *mispickel*.

**DANGEROUS CHEMICALS** — See Hazardous Chemicals.

**DANYSZ EFFECT** — The better effect realized by treating diphtheria toxin with its anti-toxin by adding it little by little with intervals, thus minimizing the quantity required for reduction of toxicity.

**" DARCO "** — A variety of decolorizing carbon made from lignite.

**DARCY EQUATION** — See Fluid Dynamics.

**DATISCIN** — See Glycosides.

**DATURIN** — See Atropine.

**D.D.T. (2,2-Bis(*p*-chlorophenyl)-1,1,1-trichloroethane)** — A white crystalline compound having the formula  $(\text{ClC}_6\text{H}_4)_2\text{CHCCl}_3$ , of m.p.  $108.5^\circ$  to  $109^\circ \text{C.}$ , and possessing high toxicity to many insect species. D.D.T. was first synthesized in 1874 by Ziedler, who condensed chlorobenzene with chloral in the presence of sulphuric acid: this method is the basis for commercial synthesis to-day. The insecticidal properties of D.D.T. were discovered by Paul Müller, working in the laboratories of the Swiss firm of J. R. Geigy, A.G., in 1936–1937. During World War II samples of insecticide mixtures were sent to England and America, where extensive research soon proved the remarkably high toxicity of the compound to many insect species. Full-scale production of the chemical was begun in 1943, and production in the United States soon reached 4,000,000 pounds per month.

D.D.T. is highly toxic to many insects, particularly those which attack man and animals, such as house flies, mosquitoes, bedbugs, lice, fleas, and gnats. It is also effective against many insects attacking crop plants, such as the codling moth, leafhoppers, flea beetles, and boll weevils. It is not effective against the Mexican bean beetle, most species of spiders, and some species of ants, for example. It is harmless to most plants, with the exception of members of the cucurbit family, such as squashes and cucumbers. It is toxic to animals, especially when in true solution in organic solvents, from which it may be absorbed through the skin. When using D.D.T. care should be taken to avoid contamination of feeds and foods; goats and cows fed on forage treated with D.D.T. may excrete the chemical in their milk.

D.D.T. is insoluble in water, but soluble in many organic solvents, such as toluene, xylene, and petroleum distillates. For insecticidal use it may be applied as a dust (mixed with an inert diluent), as a water suspension or emulsion, or in true solution. For agricultural uses the dusts are usually preferred; for household use solutions in

light petroleum fractions are commonly used. D.D.T. is also used in aerosol "bombs" from which it may be discharged under pressure as a fine mist. One of the unusual and valuable properties of D.D.T. is its residual action; deposits of crystalline D.D.T. on surfaces such as walls, floors, and screens, will kill insects which come in contact with them over a period of several months. D.D.T. is readily decomposed by alkalis, and should not be mixed with lime.

*References*: "D.D.T.: A New Insecticide," by J. W. Munro (*Nature*, **154**, 352 (1944)); "The Chemistry of DDT," by Cristol and Haller (*Chem. Eng. News*, **23**, 2070 (1945)); "The Toxicity and Potential Dangers of DDT to Humans and Warm-Blooded Animals," by Neal and von Oettingen (*Med. Ann. District of Columbia*, **15**, 15 (1946)); "Preparation of Technical DDT," by Mosher *et al.* (*Ind. Eng. Chem.*, **38**, 916 (1946)); *D.D.T.: The Synthetic Insecticide*, by West and Campbell (Chapman and Hall, London); *Chemistry of Insecticides and Fungicides* (second edition), by D. E. H. Frear (D. Van Nostrand Co., New York); also see Aerosols, "Deenate," "Gesamol," and Insecticides.

**DEACON'S CHLORINE PROCESS** — See Chlorine.

**DEAD OIL** — The "heavy oil" obtained from the distillation of coal tar.

**DEAD-SEA SALTS** — The average percentage of salts in the strong brine is given as about 25 per cent., of which 14 per cent. is sodium chloride, 4 to 7 per cent. potassium chloride, and up to 1 per cent. or more magnesium bromide. These salts and carnallite can be extracted by a staged system of evaporation and crystallization.

Magnesium chloride is the principal salt of the Dead Sea, amounting to over 50 per cent. of the total dissolved saline matter. From this source both the hydrated ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) and fused forms are obtained.

**DEARSENICATOR** — The "Trepex" dearsenicator is a superior apparatus to the old-fashioned lead tower for bringing sulphuric acid and hydrogen sulphide (as supplied by a suitable generator) into contact for dearsenication of the sulphuric acid. The gas enters at the acid outlet end and flows counter-current to the flow of the acid. The complete unit also comprises filters for removing the precipitated arsenic sulphide. The actual dearsenicator for dealing with sulphuric acid is made of cast iron, while for dealing with other acids which attack cast iron the apparatus is made of lead, timber, or ebonite. The dearsenicator is also applicable for gas-washing, and as a substitute for the Gay-Lussac tower in the "chamber" sulphuric acid process, etc.

**"DECALIN"** — See "Dekalin."

**DECAMOTHONIUM IODIDE** (C 10, "Eulissin", "Syncurine") — A colourless, odourless, crystalline compound, namely, bistrimethylammonium decane diiodide ( $\text{C}_{10}\text{H}_{38}\text{N}_2\text{I}_2$ ); soluble in water, slightly soluble in alcohol; sparingly soluble in boiling acetone, chloroform and ether; m.p.  $245^\circ$  to  $246^\circ\text{C}$ . It has been used to produce muscular relaxation in surgical anaesthesia as a substitute for *d*-tubocurarine. The chemical reactions of decamethonium iodide are described by

Balaban, Levy and Wilde in *J. Pharm. Pharmacol.*, **9**, 603 (1949). The pharmacology of curare and other curarising agents is reviewed by W. D. M. Paton in *J. Pharm. Pharmacol.*, **5**, 273 (1949). For an account of the use of decamethonium iodide in anaesthesia, see G. Organe in *Lancet*, **256**, 773 (1949). (See *d*-Tubocurarine Chloride.)

**DECANTATION** — Pouring off liquid from a deposited sediment or precipitate ; also used for partial separation of immiscible liquids.

**DECI** — Prefix signifying “ a tenth of ” in the metric system.

“ **DECICAIN** ” — See Amethocaine Hydrochloride.

**DECOCTION** — An extract of a vegetable drug, prepared by boiling with water and filtering.

**DECOLORIZERS** — See Bentonite, Bleaching, Carbon, “ Floridin,” Fuller’s Earth, Hydrogen Peroxide, Kieselguhr, and Ozone.

**DECOMPOSITION** — When a chemical compound is broken up into its constituent parts by chemical or physical means, it is said to be decomposed, the decomposition being effected by the exercise of a greater force than that of the original binding chemical affinity.

There are many ways or methods for effecting the decomposition of chemical compounds. Some can be readily decomposed by heating ; in others an electric current passed into them in a molten state or into their solutions will effect the purpose ; whilst in yet other cases mere exposure to light suffices. Acidulated water can be decomposed or broken up into hydrogen and oxygen by passing a current of electricity through it. Many silver compounds undergo chemical change when exposed to light, and practical advantage of this fact is taken in the art of photography.

Limestone is a chemical combination of lime and carbon dioxide, which, when strongly heated as in lime-kilns, is decomposed into the two parts. Some decomposition reactions are very complex, as is the case when petroleum and coal are heated to high temperatures (pyrolysis). (See Chemical Interactions, Dissociation, and Eremacausis.)

**DECORTICATION** — Shelling of seeds, previous to crushing in order to extract the oil contained in them by pressure or the action of solvents.

**DECREPITATION** — Physical rending or flying apart of the joints of the crystalline structure of certain minerals and salts when heated, attended with a crackling noise. Common salt, lead nitrate, and calcspar exhibit this behaviour. Decrepitation of barytes is attributed, in common with that of water-soluble salts, such as lead nitrate, to the content of included water ; celestine (strontium nitrate) and lead chromate also decrepitate upon heating when they contain a small quantity of water.

“ **DEENATE** ” (Du Pont) — Trade-mark for an insecticide based on D.D.T. (see Insecticides). Used for controlling insects that attack fruits and vegetables, and that infest buildings.

**DEFECATION** — Processes of purification or freeing from dregs. (See Sugar.)

**DEFLAGRATION** — Rapid combustion with evolution of light and heat, as when a strip of magnesium foil or thin iron wire is burned in oxygen gas. A mixture of nitre with antimonious sulphide, thrown into a red-hot crucible, burns with deflagration, the sulphur being oxidized by the oxygen of the nitre. A deflagration spoon is made of metal with a long handle, used to contain such substances as sulphur or phosphorus while burning.

**"DEFLUORITE"** — A specially prepared activated alumina for removal of fluoride from drinking water. The teeth of children who drink water containing fluoride (of the order of 3 parts per million or more) have the enamel mottled. See article by Gladys Swope and R. H. Hess (*Ind. Eng. Chem.*, 29, 424 (1937)).

**DEGRAS** — A crude grease obtained from sheep's wool and the tannage of chamois leathers; used in soap-making and as a leather dressing. It can also be made from fish oils, etc. (See Adeps Lanæ, and Wool.)

**DEGREASING, METAL** — Accomplished by the use of solvents, either liquid or vapour, that dissolve oils, fats, and greases. Such solvents are chlorinated hydrocarbons, paraffinic and aromatic hydrocarbons. When the vapour is used suitable means must be provided for its condensation and recovery. The recovered solvents in all cases must be recovered from the accumulated grease. Alkalis and alkaline salts, such as sodium silicate, borate, carbonate, are frequently used. (See Solvents.)

**DEHYDRATION** — The elimination of water. The water of crystallization contained in many salts is eliminated by heat; again, when alcohols are heated to from 400° to 500° C. in presence of alumina, they are decomposed into olefins and water and so forth. (See Desiccator, and Drying.)

**DEHYDROGENATION** — The removal of hydrogen from compounds by chemical means. (See Aldehydes.)

**DE-INKING** — See Paper.

**DEKA** — Prefix signifying "ten times" in the metric system.

**"DEKALIN"** (Decahydronaphthalene) ( $C_{10}H_{18}$ ) — A fully saturated hydrocarbon, used as a solvent, also as substitute for lamp, motor, and lubricating oils; devoid of optical activity, with a b.p. 193° C., flash-point 51.6° C., ref. ind. 1.4815, and sp. gr. 0.895. It is prepared by treating naphthalene in a fused state with hydrogen in the presence of a catalyst such as finely divided nickel supported and distributed on asbestos. The pressure used is about 225 lb. per sq. in., and the temperature 180° to 200° C. It is of aromatic character, with an odour something like that of camphor, and can be used as a cleansing fluid for machinery (particularly printing machines), and for removing stains from garments. As a solvent, it is stated to be equal to turpentine, and it is somewhat slower in evaporation than that liquid, which is a point

in its favour for some applications. In 1925 "Dekalin" was shown to exist in two forms, the "cis" and the "trans," thus proving what had been predicted for many years, that derivatives of decahydronaphthalene should exhibit a special form of geometrical isomerism. (See Isomerism, and "Tetralin.")

**DELIQUESCENT** — Absorption of moisture from the air, whereby substances become pasty or more or less liquid in character; for example, calcium chloride is very deliquescent, as is also magnesium chloride, the presence of small proportions of which in common salt causes the latter to become moist. The phenomenon of deliquescence is dependent upon the relation between the absolute water vapour pressure of air and the absolute water vapour pressure of a solution of the substance in question by condensation of water vapour on the substance, the vapour pressure of its solution being below that of atmospheric aqueous vapour.

Some crystalline substances when exposed to the air combine with the moisture contained therein and pass into other distinct crystalline forms; in certain instances the combination continues to such an extent that the substance liquefies. (See Drying-Tubes, and Efflorescence.)

**DELPHINIDINE** ( $C_{15}H_{11}O_7N$ ) — An anthocyanidin pigment obtained by hydrolysis from a glycoside occurring in the purple larkspur and the blue-black pansy. It has been synthesized. (See *Organic Chemistry*, by Gilman (John Wiley and Sons, New York).)

**DELPHININE (Delphinin)** ( $C_{33}H_{45}O_9N$ ) — A white, crystalline, poisonous alkaloid, soluble in alcohol and ether, contained in stavesacre seeds from the herb *Delphinium staphisagria*, or larkspur; formerly used in ointment or lotion form to destroy *pediculi*.

**DENATURANTS** — Substances introduced into alcohol, made for general use and industrial purposes, to prevent its consumption as drink—such as wood alcohol, paraffin oil, pyridine, camphor, naphtha, nitrobenzol, pine oil, benzene, and liquid diethylphthalate. (See Methylated Spirits.)

**DENATURED ALCOHOLS** — See Denaturants, and Methylated Spirits.

**DENITRATION** — (1) The removal of nitrogen oxides from sulphuric acid; (2) the removal or change of the nitro group ( $-NO_2$ ) in organic compounds.

**DENSITIES** — (See **Elements for data for individual elements**.) Mass (weight) per unit volume. Water is taken as a standard of comparison for liquids and solids, whilst hydrogen or air is ordinarily taken as that of gases. The critical density of a fluid is its density in the critical state, being the reciprocal of its critical volume. (See Critical Point, Gases, Hydrometer, Molecules, and Specific Gravities.)

**DENTINE** — The exposed parts of the teeth (which on the whole have a bone composition), consisting of a combination of calcium and magnesium compounds and organic matter of a gelatinous character.

The following analysis is one of human teeth :

Phosphate and fluoride of calcium	..	..	66.7 per cent.
Calcium carbonate	..	..	3.4 "
Magnesium phosphate	..	..	1.0 "
Salts	..	..	0.83 "
Fat	..	..	0.40 "
Organic matter	..	..	28.00 "

**DEOXIDATION** — The removal of oxygen as a constituent of a substance ; for instance, iron oxide is deoxidized by heating with carbonaceous material, as in smelting, thus reducing it to the metallic state. Barium dioxide is partially deoxidized to the state of barium monoxide by heating it to a high temperature.

**DEOXYCORTONE ACETATE (Desoxycorticosterone Acetate, "D.O.C.A.," "Percorten")** — A colourless, odourless, crystalline compound, being the acetate of  $\Delta^4$ -21-hydroxypregnen-3,20-dione, one of the hormones secreted by the suprarenal cortex. It may be prepared synthetically from stigmasterol or cholesterol by oxidative degradation. It is insoluble in water but soluble in alcohol, acetone and fixed oils ; m.p. about  $156^\circ\text{C}$ . It is used in medicine for the treatment of Addison's disease, for which purpose it is injected as a sterile solution in oil or implanted in the tissues in the form of a sterile pellet. Since the discovery that arthritis may be treated by injections of cortisone, another hormone of the suprarenal cortex, deoxycortone acetate has been used, in combination with ascorbic acid, for the treatment of this condition with varying degrees of success.

The preparation of deoxycortone acetate is described in F.I.A.T., Final Report No. 996 and B.I.O.S., Final Report No. 449. An improved method of preparation is described by A. L. Wilds and C. H. Shunk, *J. Amer. Chem. Soc.*, **70**, 2427 (1948). See also Kuizenga, *The Chemistry and Physiology of the Hormones* (Amer. Assoc. Adv. Sci., 1944). Its use in medicine is described by Thorn *et al.*, *Ann. Int. Med.*, **16**, 1053 (1942). The use of deoxycortone acetate in the treatment of arthritis is described by Lewin and Wassen, *Lancet*, **2**, 993 (1949). (See Cortisone.)

**DEPHLEGMATE** — To deprive of water or other liquids by evaporation or distillation, using for fractional separation a fractionating column or dephlegmator. The dephlegmator is so constructed that the vapour from the still is made to pass through several successive layers of the condensed distillate before reaching the condenser, thus increasing the efficiency of the fractional separation of any lower boiling constituent. (See Distillation.)

**DEPILATORIES** — Chemicals used for the removal of hair, the most commonly used being the sulphides of the alkali metals which are used in tanning operations. Thallium acetate ( $\text{CH}_3\text{COOTl}$ ) has been used as a depilatory in the treatment of ringworm of the scalp, but because of the risks of toxic effects, it has largely been replaced by the use of X-rays. Superfluous hair may also be removed by means of diathermy and electrolysis.

**DEPOLARIZE (Electrical)** — To remove polarization in an electrical cell by the chemical action of added substances such as manganese dioxide, which reacts with the hydrogen liberated at the cathode and thus effects the desired change.

**"DERBY RED"** — Trade name for basic lead chromate; the deeper shades are also known as "Chinese" or "Persian" reds.

**DERBYSHIRE SPAR** — See Fluorine.

**DERMATOL** — See Bismuth Subgallate.

**"DEROBIN"** — See Dithranol.

**DERRIS ROOT** (*Derris elliptica*) is cultivated in Borneo, Java, Sumatra, and Straits Settlement. Four so-called active constituents have been isolated, namely, rotenone, deguelin, toxicarol, and tephrosin. (See A. M. Ambrose and H. B. Haag on "Toxicological Studies of Derris" (*Ind. Eng. Chem.*, **29**, 429 (1937)); "The Constituents of Derris and Other Rotenone-Bearing Plants," by Haller *et al.* (*Chem. Rev.*, **30**, 33 (1942)); *Chemistry of Insecticides and Fungicides*, by Frear (D. Van Nostrand Co., New York); *Insecticides*, and *Rotenone*.)

**DESICCATE** — To dry or denude of water. (See Drying.)

**DESICCATOR** — A drying appliance designed to effect dehydration, that is, the removal of water from chemical substances. A common form consists of a perforated shelf on which the material to be dried can be placed in its containing vessel and the drying-agent is stored beneath the shelf. The whole is covered air tight by a greased ground glass cover. The temperature may be controlled when necessary by proper storage. The pressure may be lowered in the desiccator by attachment of vacuum to a stop-cock outlet. (See Air-Pump, and Drying.)

**"DESICHLORA"** — Barium perchlorate ( $\text{Ba}(\text{ClO}_4)_2$ ) prepared for use as a reagent for the removal of water vapour from gases.

**DESOXYCORTICOSTERONE ACETATE** — See Deoxycortone Acetate.

**DESOXYCORTONE ACETATE** — See Deoxycortone Acetate.

**DESTRUCTORS** — There are various makes and types of destructors available, among other purposes, for the utilization of factory refuse by way of fuel economy—for example, the "Horsfall" destructors, one of which is made to burn "washery" refuse from collieries, and the "Meldrum" destructor; while for burning mixed refuse there are larger appliances, such as the "Heenan" and the "Heenan and Froude" destructors. Wastes that can be ground up with water may be so disposed of.

**DETERGENTS** — The best-known detergents are the soaps (see same), but these have many drawbacks, not the least of which is the scum they produce with hard water, and so for many purposes they are being replaced with synthetic detergents. The shortage of fats caused by World War II gave a further impetus to the search for "soap substitutes."

The first substance of this nature to be used on a considerable scale was the well-known turkey-red oil (see same), the efficacy of which depends on the presence of the grouping  $\text{ROSO}_2\text{ONa}$ , where R is a hydrocarbon chain. This grouping is present in most of the modern **Anionic** detergents, such as "Teepol" and "Gardinol," which are produced by the sulphation of olefines and the neutralization of the resulting acid esters. Another type of anionic detergent is the sodium alkyl-aryl sulphonates of the general formula  $\text{R.C}_6\text{H}_4.\text{SO}_2\text{ONa}$ , such as "Permal W."

The **Non-Ionic** detergents contain a chain of ether linkages, such as  $\text{R(OC}_2\text{H}_4)_n\text{OH}$ , of which "Lissapol N" is an example.

The **Cationic** detergents are salts of the tetrasubstituted ammonium ion, such as "Cetavlon," which is cetyltrimethyl ammonium bromide. This type are sometimes called "invert soaps."

None of these types of detergents form insoluble calcium or magnesium salts, and can therefore be used with hard water, which is a great asset in laundering and dyeing. Apart from these industries, which absorb by far the greater proportion of synthetic detergents, they also find use in the leather, textile, and fur trades, shampoos, on ships at sea since they are compatible with salt water, to reduce dust in mines, and in medicine and pharmacy, and in the cosmetic industries. Since most of these products depend on petroleum instead of on fats, their increased use will eventually release more edible fats and oils for human consumption.

*References:* *The Fundamentals of Detergency*, by W. W. Niven (Reinhold Publishing Corp., New York); *Surface Active Agents*, by C. B. F. Young and K. W. Coons (Chemical Publishing Co., Brooklyn); *Surface Active Agents. Their Chemistry and Technology*, by A. M. Schwartz and J. W. Perry (Interscience Publishers, New York); *Surface Tension and the Spreading of Liquids*, by R. S. Burdon (Cambridge University Press).

**DETONATORS** — Copper tubes containing a charge of mercuric fulminate alone or mixed with potassium chlorate or other ingredients. Other detonating compounds include a trinitrophenylmethylnitramine known as "Tetryl", tetranitroaniline, cyanuric triazide, lead azide, etc. Detonation requires to be started by a strong impulse such as that imparted by the explosion of a charge of mercury fulminate; it proceeds very rapidly from layer to layer, and is due to the formation of an explosion wave having a velocity of thousands of metres per second; that for  $2\text{H}_2 + \text{O}_2$  is 2,810 metres per second. In blasting operations detonators (like gunpowder) are either fired by a time-fuse or electrically. As a primer for detonators, lead azide is much cheaper than fulminate of mercury. According to L. V. Clark, diazodinitrophenol is less sensitive to impact and storage than mercury fulminate or lead azide (see *Ind. Eng. Chem.*, 25, 663 (1933)). (See Azides, and Explosives.)

**DETRITUS** — Redeposited matter worn off rocks.

**DEUTERIUM** — See Hydrogen (Heavy).

**DEUTERON** — The nucleus of the deuterium (heavy hydrogen) atom of mass 2, charge 1 negative. Used as an important particle in nuclear bombardment.

**" DEVEGAN "** — See Acetarsol.

**DEVITRIFICATION** — See Glass.

**" DEVOLITE "** — A proprietary brand of colloidal clay of use in the rubber, paint, and toilet articles industries.

**DEWAR FLASK** — See Vacuum.

**DEW-POINT** — The temperature at which the atmospheric air is saturated with moisture and begins, in consequence, to deposit it. (See Air.)

**" DEXONITE "** — A substitute for vulcanite and ebonite as an insulating material ; non-corrosive and acid-resisting ; sp. gr. at 60° F. 1.2765.

**DEXTRAN** — A polysaccharide composed entirely of dextrose units, produced when the non-pathogenic coccus, *Leuconostoc mesenteroides*, is cultured in a substrate of sucrose and phosphate. Dextran is formed from sucrose by the action of an enzyme or enzymes produced by the micro-organisms. After removal of the protein and inorganic salts from the culture medium, dextran is precipitated with organic solvents such as acetone. It is composed of dextrose units, each joined by an *alpha*-glycosidic linkage to the primary alcoholic hydroxyl group of its neighbour. There may also be occasional branch linkages through other secondary alcoholic hydroxyl groups. Undegraded dextran, prepared in this way, was tested in Sweden as a synthetic substitute for plasma in the preparation of transfusion fluids to replace blood. It was found that the molecules were too large for this purpose, but more encouraging results were obtained by samples in which the average size of the molecules had been reduced by partial hydrolysis with acid. (See G. Thorsen, *Lancet*, 1, 132 (1949) ; and J. P. Bull *et al.*, *ibid.*, 1, 134 (1949).)

**DEXTRIN (British Gum, Starch Gum)** — The comprehensive name given to the varying dextro-rotatory, gummy, intermediate, hydrolytic products, including maltose and *d*-glucose, obtained from starch by heating with or without the supplemental help of acids, alkalis, or diastase. Ling and Nanji have shown that so-called stable dextrin can be obtained in almost theoretical yield from the products of the action of malt diastase on starch at 40° C. as a white powder which is acted on slowly by maltase to form *isomaltose*, and by emulsin, giving *isomaltose* and dextrose. In the commercial manufacture, acid is usually employed, and the procedure varied according to the nature of the dextrine or gum required.

The dextrines are soluble in water, do not reduce Fehling's solution, and are not fermentable. They are largely used in the sizing of white goods, manufacture of foods, and as adhesives. By a patented method it is claimed that great adhesive strength is given to a solution of 800 grams dextrine dissolved in a litre of water by the addition of 200 grams calcium nitrate. (See Glucose, and Starch.)

**DEXTRO-ROTATORY** — See Polarization.

**DEXTROSE** — See Glucose.

**DHOL** — A dried lentil of various types produced in India.

**DIABANTITE** — An uncommon member of the chlorite group of complex mineral silicates.

**DIACETINE** — See Acetin, Triacetin, and Glycerol.

**" DIAL "** — See Allobarbitone.

**DIALYSIS** — A sort of diffusion by means of which a liquid which contains, say, a crystallizable substance such as salt or sugar, with another which is not crystallizable (colloid), such as albumin or gum, can be separated. This is effected by placing the mixture in a tray or other vessel having as its boundary a sheet of parchment paper or animal membrane, such as bladder, etc., and floating or suspending this vessel in a dish of water, when the crystallizable substance (dialysate) in solution dialyses or diffuses through the parchment boundary into the water outside, and the colloidal substance in solution remains behind in the containing vessel. Colloidal solutions are not utterly devoid of the property of diffusion, but as the size of the constituent particles is great in comparison with that of the molecules, they diffuse very slowly as compared with crystalloids. Incidentally, it may be remarked that there are dialysers specially made for the recovery of soda-lye in viscose factories amongst other applications. (See Colloid Chemistry, and Osmosis.)

**DIAMIDE** — See Hydrazine.

**DIAMINES** — Organic compounds containing two amino groups, such as ethylene diamine ( $C_2H_4(NH_2)_2$ ), a colourless liquid of ammoniacal odour, sp. gr. 0.892, b.p.  $116.5^\circ C$ . (See Amines.)

**DIAMINOPHENOL** ( $C_6H_3(OH)(NH_2)_2$  (1, 2, 4)) — The commercial varieties of this substance are greyish-white and crystalline, soluble in alcohol, and used as photographic developers. (See Amidol.)

**DIAMOND** — See Carbon.

**DIAMORPHINE** (Diacetylmorphine, Heroin) ( $C_{21}H_{23}O_5N$ ) — A white, crystalline alkaloid obtained by acetylation of morphine; soluble in hot alcohol and ether; m.p.  $171^\circ C$ . It is used in medicine in the form of its hydrochloride which melts between  $229^\circ$  and  $233^\circ C$ ., and is soluble in water. Preparations of diamorphine are used as sedatives and narcotics and are included in the schedule of dangerous drugs the distribution of which is subject to international control.

**DIAPHANOUS** — Transparent to light.

**DIAPHRAGM** — A semi-permeable membrane used in dialysis in the form of parchment, and in electrolytic cells in the form of asbestos. (See Dialysis, Osmosis, and Porosity.)

**DIASONE** — The disodium salt of diaminodiphenylsulphone formaldehyde sulphoxylate ( $\text{SO}_2(\text{C}_6\text{H}_4.\text{NH}.\text{CH}_2.\text{SO}_2\text{Na})_2.4\text{H}_2\text{O}$ ) ; soluble in water but becoming insoluble owing to oxidation if exposed to the atmosphere. The addition of 10 per cent. of sodium bicarbonate acts as a stabilizer. It has been shown to be active against experimental infections with tuberculosis in animals and is less toxic than "Promin". Its use in the treatment of tuberculosis, however, has proved disappointing. It has also been used for the treatment of leprosy. The synthesis of Diasone is described by Bauer, *J. Amer. Chem. Soc.*, **61**, 617 (1939) ; and by Raiziss, *J. Amer. Pharm. Ass.*, **33**, 43 (1944). An account of its use in the treatment of tuberculosis is given by Pfuete and Pyle, *Diseases of the Chest*, **11**, 213, 220 (1945) ; and in leprosy by Faget, *Pub. Hlth. Rep.*, **61**, 960 (1946). (See "Promin", "Promizole" and "Sulphetrone.")

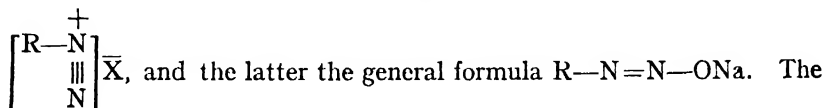
**DIASPORE** — Mineral alumina of composition  $\text{Al}_2\text{O}_3.\text{H}_2\text{O}$ , crystal system No. 4, and sp. gr. 3.5.

**DIASTASE** — An amorphous active principle or enzyme, soluble in water, contained in extract of malt, and capable of turning starch into soluble substances susceptible of fermentation. According to a patented method, diastase is formed by growing *Aspergillus oryzae* upon the residue from germinated barley or wheat, alone or mixed with bran or corn from which the starch has been removed. The diastase is extracted with water or with a mixture of water and alcohol or glycerine, and precipitated from the extract with any known precipitant. It loses its activity at temperatures above  $70^\circ\text{C}$ . (See Beer, *Enzymes*, Malt, and Starch.)

**DIATHERMANOUS** — A characteristic of substances like rock-crystal which transmit heat waves as transparent substances transmit light waves.

**DIATOMITE (Diatomaceous Earths)** — Forms of kieselguhr or siliceous deposits containing water, organic matter, and other impurities of varying amounts. (See monograph on the subject issued by the Imperial Institute (H.M. Stationery Office) ; also *Diatomaceous Earth*, by Robert Calvert (Reinhold Publishing Corp., New York) ; Kieselguhr, Silicon, and Tripoli.)

**DIAZO GROUP**, a bivalent group ( $-\text{N}_2-$ ), the highly reactive grouping in the aryl diazonium salts, and their sodium and potassium diazoate derivatives. The former compounds possess the general formula



diazonium compounds are prepared from primary aromatic amines by the process known as **Diazotization**, in which the amine is treated in acid solution (usually ice-cold) with a solution of sodium nitrite. These compounds are extremely important in synthetic organic chemistry and the dye industry.

**DIBASIC** — See Basicity, and Valencies.

**DIBUTYL PHTHALATE** ( $C_6H_4(COOC_4H_9)_2$ ) — A high-boiling organic solvent, of sp. gr. 1.047, b.p.  $340^\circ C.$ , ref. ind. 1.490, flash point  $360^\circ F.$ , immiscible with water. It is an important plasticizer, and is also used in melting-point apparatus on account of its high boiling and flash points.

**DICHLORANILINE** — A dye intermediate. (See Chloranilines.)

**DICHLORBENZIDINE** ( $C_6H_3(Cl)NH_2.C_6H_3(Cl)NH_2$ ) — A crystalline intermediate soluble in alcohol and ether.

**DICHLOROBENZENE** ( $C_6H_4Cl_2$ ) — Para-dichlorobenzene is a white crystalline intermediate, m.p.  $53^\circ C.$  and b.p.  $174^\circ C.$ ; used also as an insecticide for peach-borer (*Aegeria exitiosa*) control in Georgia and elsewhere and as a moth-preventive. The ortho-compound also finds several industrial applications, in cleaning, as a fat solvent and spray for clothes moths, etc.

**DICHLORODIETHYLETHER** ( $CH_2Cl.CH_2O.CH_2.CH_2Cl$ ) — An important solvent, b.p.  $178^\circ C.$ , insoluble in water, but soluble in alcohol and ether, used as a constituent of liquid textile soaps, as solvent in the refining of petroleum lubricating oils, as a cleaning agent for metal, and for general use. (See Page *et al.* on "Production of Lubricating Oils by Extraction with Dichlorodiethyl Ether" (*Ind. Eng. Chem.*, **25**, 418 (1933)); and "Chlorex".)

**DICHLOROETHANE** ( $CH_3.CHCl_2(1, 1)$ ) (Ethidene Chloride, Ethylidene Chloride) — A by-product in the manufacture of chloral, possessing anæsthetic properties; b.p.  $57^\circ C.$ ; also prepared by the further chlorination of  $C_2H_5Cl$ .

**DICHLOROETHANE** ( $CH_2Cl.CH_2Cl(1, 2)$ ) — See Ethylene Dichloride.

**DICHLOROETHYLENE** — See Solvents.

**DICHLOROHYDRIN** (Glycerol Dichlorohydrin; 1, 3-Dichloropropanol-2) ( $CH_2Cl.CHOH.CH_2Cl$ ) — A colourless liquid, sp. gr. 1.367, b.p.  $174^\circ C.$ , soluble in alcohol and ether, prepared by interaction of dry hydrochloric acid gas and glycerine, followed by distillation; used as a solvent of nitrocellulose and resins, and for making photographic lacquers, etc.

**DICHOISM** — The property possessed by double-refracting crystals of exhibiting two colours when viewed in different directions. (See Crystals, and Fluorescence.)

**DICOPHANE** — See D.D.T.

**DICOUMAROL** (Dicoumarin) ( $C_{19}H_{12}O_6$ ) — A white, crystalline substance, namely, 3,3-methylenebis (4-hydroxycoumarin), occurring in spoiled sweet clover and prepared by the action of formaldehyde on 4-hydroxycoumarin; sparingly soluble in water; m.p.  $286^\circ$  to  $289^\circ C.$  Its presence in clover hay was found to be the cause of hæmorrhagic disease in cattle (see M. A. Stahmann, C. F. Huebner, and K. P. Link, *J. Biol. Chem.*, **138**, 513 (1941)). It is used in medicine to prolong the clotting time of blood and probably exerts its effect by inhibiting the

formation of prothrombin in the liver. It has a much more prolonged action than heparin, the anticoagulant principle extracted from liver (see J. Lehmann, *Lancet*, 1, 318 (1942)).

**DICYANDIAMIDE** — A grey-white crystalline product used as a fertilizer, prepared by the hydrolysis of calcium cyanamide ( $2\text{CaCN}_2 + 4\text{H}_2\text{O} = 2\text{Ca(OH)}_2 + (\text{CN.NH}_2)_2$ ) or by heating it to  $150^\circ\text{C}$ .

**DIE-CASTING** — Technique of producing accurately dimensioned parts by forcing molten metal under pressure into metal dies or moulds. Aluminium, copper, lead, magnesium, tin, and zinc alloys are commercially employed for this purpose. Machines are available which die cast automatically at the rate of 500 parts per hour. The technique is very economical for mass production. (See *Die Casting for Engineers*, by New Jersey Zinc Co., New York.)

**DIELDRIN** (1, 2, 3, 4, 10, 10-Hexachloro-6, 7-epoxy-1, 4, 4a, 5, 6, 7, 8, 8a-octahydro-1, 4, 5, 8-dimethano-naphthalene) — An insecticide.

**DIELECTRIC CONSTANT** — The electro-static force mutually exercised between two electrically charged bodies varies with the medium employed, and the measure of this property constitutes the dielectric constant. The unit is the dielectric constant of a vacuum; the constant for air at  $20^\circ\text{C}$ , 1 atm., is 1.00058, and for glass and sulphur 3. The dielectric constants of various liquids are shown in the accompanying table.

DIELECTRIC CONSTANTS OF VARIOUS LIQUIDS AT  $20^\circ\text{C}$ .

Liquid	Dielectric Constant At $20^\circ\text{C}$ .	Liquid	Dielectric Constant At $20^\circ\text{C}$ .
Hydrogen cyanide ..	116	Ammonia .. ..	15.5
Water .. ..	80	Sulphur dioxide ..	12.4
Glycerol .. ..	56	Acetic acid .. ..	9.7
Nitromethane .. ..	39	Phenol .. ..	9.7
Methyl nitrile .. ..	37	Ethyl bromide ..	9.5
Nitrobenzene .. ..	36	Aniline .. ..	7.0
Methyl alcohol .. ..	33	Ethyl amine .. ..	6.3
Isopropyl alcohol ..	26	Hydrogen sulphide ..	5.7
Ethyl alcohol .. ..	25	Chlorobenzene ..	5.6
Acetaldehyde .. ..	21.6	Chloroform .. ..	5.1
Acetone .. ..	21.4	Castor oil .. ..	4.7
n-Butyl alcohol .. ..	16	Hydrogen chloride ..	4.6
n-Amyl alcohol .. ..	16	Ethyl ether .. ..	4.3

"DIELINE" — See Solvents.

**DIENŒSTROL** ( $C_{18}H_{20}O_2$ ) — A synthetic, crystalline compound, namely, 2,4-di(*p*-hydroxyphenyl)-2,4-hexadiene; insoluble in water; soluble in fixed oils. It is one of a series of synthetic œstrogens which possess activity similar to œstradiol, the female sex hormone, and is used in medicine for the treatment of conditions due to hormonal deficiency and for prostatic carcinoma. Dienœstrol has been stated to be more active than stilbœstrol, the first of the compounds of this type to be introduced into medicine, but this has not been proved by clinical experience (see E. C. Dodds, *J. Pharm. et Pharmacol.*, **3**, 137 (1949)). (See Œstradiol, and Stilbœstrol.)

**DIESEL OIL** — In the diesel engine the fuel is ignited by the heat of compression, and the most valuable fuel characteristic is a low spontaneous ignition temperature. High-grade diesel oils therefore have a high *cetane number* (see Cetane Rating), which corresponds to a low spontaneous ignition temperature.

The following specifications represent grades of diesel oil on the British market. The first is for automotive and high-speed engines, the second for large slow-running marine and stationary engines.

	Distillate Diesel Oil	Marine Diesel Oil
Specific gravity at 60° F. .. ..	about 0.85	0.920 max.
Flash point (closed) .. ..	150° F. min.	150° F. min.
Viscosity, Redwood 1 at 100° F. ..	32/40 sec.	36/70 sec.
Pour test .. ..	20° F. max.	25° F. max.
Cetane Number .. ..	45 min.	28 min.
Water content .. ..	0.05% max.	0.25% max.
Sediment content .. ..	0.01% max.	0.1% max.

Specifications of the Bureau of Engineering, U.S. Navy, are as follows :

Flash point, closed cup .. ..	150° F. min.
Pour point .. ..	0° F. max.
Viscosity, Saybolt Universal .. ..	35–45 at 100° F.
Water and sediment .. ..	0.05% max.
Total sulphur .. ..	1.0% max.
Carbon residue .. ..	0.1% max.
Ash .. ..	0.01% max.
Corrosion, copper strip .. ..	Negative at 212° F.
Colour, A.S.T.M. .. ..	5 max.
Ignition quality, cetane number .. ..	50 min.

In *Diesel Fuel Oils. Production, Characteristics, and Combustion*, by Amer. Soc. Mech. Eng., New York, 1948, the carbon monoxide content of the exhaust gas from Diesel engines is related to the fuel to air ratio as follows :

Carbon Monoxide Volume Per Cent.	Ratio : $\frac{\text{Pounds of Fuel}}{\text{Pounds of Air}}$
6.0	0.09
3.0	0.08
1.0	0.07
0.5	0.067 (Chemically correct ratio)
0.1	0.057
0.03 (Minimum value)	0.03
0.04	0.015

**DIET** — See Feeding Stuffs, and Foods.

**DIETHYLAMINE**  $((\text{C}_2\text{H}_5)_2\text{NH})$  — A volatile inflammable liquid, sp. gr. 0.712 and b.p.  $55.5^\circ\text{C}$ ., prepared by action of dilute potassium hydroxide on 3-nitrosodiethylaniline. (See Amines.)

**DIETHYLANILINE**  $(\text{C}_6\text{H}_5.\text{N}(\text{C}_2\text{H}_5)_2)$  — A yellowish-brown, inflammable liquid of sp. gr. 0.934 obtained by heating a mixture of aniline, aniline hydrochloride, and ethyl alcohol. It boils at  $216^\circ\text{C}$ ., is soluble in alcohol and ether, and employed in the manufacture of "brilliant green" and other synthetic dyes.

**DIETHYL SULPHATE**  $((\text{C}_2\text{H}_5\text{O})_2\text{SO}_2)$  — A colourless, non-poisonous, non-inflammable liquid of faint ethereal odour, sp. gr. 1.172, and b.p.  $208^\circ\text{C}$ . It begins to decompose slowly above  $150^\circ\text{C}$ ., and deposits crystals upon cooling to  $-24.5^\circ\text{C}$ . Upon boiling with water (with which it is non-miscible) it is hydrolysed into ethyl alcohol and sulphuric acid. It is used for the ethylation of organic substances, and in the preparation of ethyl chloride, bromide, and iodide. It is prepared by the vacuum distillation of the product obtained by mixing ethyl alcohol and sulphur trioxide. It is not toxic, as is the corresponding dimethyl sulphate, which is used for introducing the methyl group.

**DIETHYLSTILBÆSTROL** — See Stilbæstrol.

**DIFFUSION** — When a small sample of hydrogen sulphide is opened in a room it is not long before it can be smelled in all parts of the room—the hydrogen sulphide has diffused, due to its kinetic motion, throughout the room. All gases and vapours show this behaviour to a greater or less degree. If two aqueous solutions of different density are placed together they will diffuse one into the other due to the kinetic motion of the molecules.

Graham, in 1832, showed that for gases and vapours the relative rates of diffusion ( $r$ ) are inversely proportional to the square root of the molecular weights ( $M$ ) or densities ( $d$ ), *i.e.*,

$$\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

Hydrogen, being the lightest gas, diffuses faster than any other gas.

Solutions will diffuse one into another, if miscible, at a rate depending upon the difference in concentration at the boundary between the solutions.

Gases will diffuse through thin porous plates of metal or ceramic construction, for example, hydrogen will diffuse through nickel. The rate at which several gases diffuse through porous solids is governed by Graham's law. In a like manner isotopic forms of the same gas should show a differential rate in diffusing through porous solids due to their differences in mass. The greater the ratio of the masses of the two forms the more efficient will be the separation. Consequently diffusion methods are more effective in separating isotopes of light elements than of heavier elements, for example, the rates at which hydrogen, atomic weight 1, and hydrogen, atomic weight 2, diffuse will be

$$\frac{r_1}{r_2} = \frac{\sqrt{4}}{\sqrt{2}} = \sqrt{\frac{2}{1}} = 1.42$$

but for chlorine atomic weight 35 and chlorine atomic weight 37

$$\frac{r_{35}}{r_{37}} = \frac{\sqrt{74}}{\sqrt{70}} = 1.025.$$

The process of gaseous diffusion has gained notoriety in the concentration of uranium atomic weight 235 from uranium atomic weight 238 using uranium hexafluoride as the diffusing gas and some thousands of porous membranes for barriers.

Diffusion between solid bodies can take place very slowly. It has been shown that when an alloy of lead and gold is pressed tightly against pure lead at 165° C. for 30 days, some gold passes into the lead. Gold will also diffuse into silver; copper into nickel; and copper into zinc.

*References:* *Textbook of Physical Chemistry*, by Glasstone (D. Van Nostrand Co., New York).

**DIGEST** — To steep in or expose a substance to the digestive action of a solvent liquid.

**DIGESTER** — See Autoclave.

**DIGESTION (Animal)** — See Bile, Chyle, Chyme, Gastric Juice, Pancreatic Juice, and Saliva.

**DIGITALIS** — A genus of plants belonging to the Scrophulariaceae, occurring widely in England and Europe and containing a number of glycosides which have a specific action on the heart. The drug commonly used in medicine consists of the powdered dried leaf of *Digitalis purpurea* which is standardized biologically and may also be used to prepare an alcoholic tincture. It contains a mixture of glycosides which can be separated into deacetyllanatoside A, deacetyllanatoside B and gitalin. On further hydrolysis by enzyme action, deacetyllanatoside A yields the glycoside, digitoxin and glucose. Deacetyllanatoside B

can similarly be split up into gitoxin and glucose. On acid hydrolysis, digitoxin yields the aglycone, digitoxigenin, and three molecules of a pentose sugar called digitoxose. Gitoxin is similarly composed of gitoxigenin and three molecules of digitoxose, whilst gitalin contains the aglycone, gitaligenin, in combination with two molecules of digitoxose. All the aglycones of the digitalis glycosides have a common steroid structure. See A. Stoll, *The Cardiac Glycosides* (Pharmaceutical Press, London) (1937).

Another important source of digitalis glycosides is *Digitalis lanata* which contains a mixture of active principles (digidanid) differing slightly from those of *D. purpurea*. Digidanid can be separated into three main constituents, namely, lanatoside A, B and C. On mild alkaline hydrolysis, lanatoside A and B yield deacetyl lanatoside A and B respectively and these correspond to the constituents of *D. purpurea*. Lanatoside C, on mild alkaline hydrolysis, yields deacetyl lanatoside C, which by enzymatic hydrolysis, can be split into digoxin and glucose. On further acid hydrolysis, digoxin forms digoxigenin and three molecules of digitoxose.

**Lanatoside C** ( $C_{49}H_{78}O_{20}$ ) is a pure crystalline substance, soluble in methyl or ethyl alcohol, slightly soluble in water; m.p.  $245^{\circ}$  to  $248^{\circ}$  C.

**Digitoxin** (Digitaline Crystallisée) ( $C_{41}H_{64}O_{13}$ ) is practically insoluble in water, sparingly soluble in ether and soluble in alcohol and chloroform; m.p. between  $253^{\circ}$  and  $263^{\circ}$  C. Most commercial samples contain a small amount of gitoxin and other related glycosides.

**Digoxin** ( $C_{41}H_{64}O_{14}$ ) occurs as a white crystalline substance, sparingly soluble in water, soluble in alcohol; m.p.  $265^{\circ}$  C. with decomposition. For medical purposes, it is preferred to preparations of *D. purpurea* since, being a pure chemical entity, it can be standardized by chemical means and does not require biological standardization. See *Digitalis and Other Cardiotonic Drugs*, by E. R. Movitt (Oxford Medical Publications, New York) (1946).

**DIGITONIN** — See Digitalis.

**DIGLYCOLIC ACID** (Du Pont) ( $COOH.CH_2.O.CH_2.COOH$ ) — A white crystalline solid, of m.p.  $148^{\circ}$  C., soluble in water and in ethanol. Used in the manufacture of resins and plasticizers, and in organic syntheses.

**DIHYDROROTENONE** — Formed by the hydrogenation of rotenone using a nickel catalyst in ethyl acetate solution at room temperature and at atmospheric pressure; equals or surpasses rotenone in toxicity towards insects, and more stable to oxidation than rotenone when exposed on foliage. (See H. L. Haller and P. S. Schaffer, *Ind. Eng. Chem.*, **25**, 983 (1933).)

**DIHYDROSTREPTOMYCIN** — See Streptomycin.

**DIKA BUTTER (Cay-Cay Butter)** — Obtained from the kernels of certain species of the oil-bearing *Irvingia*. The product obtained from *Irvingia gabonensis* of Africa is known as dika butter, while the *I. oliveri* of Asia gives a similar product called cay-cay butter.

Dika butter melts at 38.9° C., has a sp. gr. of 0.914 at 40° C., a sap. v. of 244.5, and i.v. 5.2. It contains mainly lauric and myristic acids and a small percentage of oleic acid; has edible value, and is of some importance in the chocolate industry, and can be used in soap and candle making, etc. The residual cake resembles copra cake, and can be used for animal consumption.

**DILL-SEED OIL** — A pale yellow volatile oil obtained by distillation from the fruit of *Anethum graveolens*, cultivated in England, Germany, East India and U.S.S.R. It contains 40 to 60 per cent. of carvone ( $C_{10}H_{14}O$ ) together with limonene and other terpenes; sp. gr. 0.900 to 0.915 at 15° C.; opt. rot. +70° to +80° at 20° C.; ref. ind. 1.481 to 1.492 at 20° C. It is used in medicine as a carminative and as a flavouring agent.

East Indian dill oil, obtained from the fruit of *Peucedanum sowa*, has a higher specific gravity (0.948 to 0.975) and contains dill apiol which is heavier than water and boils at about 285° C.

**DILUENTS** — Liquids used for diluting or thinning solutions by addition thereto, for example, various hydrocarbons such as turpentine, benzol, gasoline are added to paints and lacquers to attain the desired consistency and drying rates.

**DILUTION LAW (Ostwald's)** — See Solution.

**DIMERCAPROL (B.A.L., British Anti-Lewisite)** ( $CH_2(SH).CH(SH).CH_2OH$ ) — A colourless oily liquid, namely, 2,3-dimercaptopropanol, prepared by treating 2,3-dibromhydrin with sodium hydrogen sulphide; soluble in water to the extent of 6 per cent.; readily soluble in fat solvents. It was developed in wartime as an antidote to arsenical poison gases and a 5 per cent. solution in olive oil and benzyl benzoate is now used in medicine for the treatment of arsenical, mercurial, and gold poisoning following therapy with these metals.

An account of the original work on this substance is given by R. A. Peters, L. A. Stocken, and R. H. S. Thompson, *Nature* (London), 156, 616 (1945). A report of its use in arsenical intoxication has been published by the Medical Research Council, *Brit. Med. J.*, 1947, 520. For the clinical and biological aspects, see R. H. S. Thompson and V. P. Whittaker, *Biochem. J.*, 41, 342 (1947); L. A. Stocken, *ibid.*, 41, 358 (1947). For an account of its manufacture, see L. A. Stocken, *J. Chem. Soc.*, 1947, 592.

**DIMETHYLAMINE** ( $(CH_3)_2NH$ ) — The simplest secondary amine, of b.p. 7.4° C. Produced by the action of alkalis on *p*-nitrosodimethylaniline. It occurs naturally, with methylamine in herring brine. (See Amines.)

**DIMETHYLANILINE** ( $C_6H_5N(CH_3)_2$ ) — A tertiary amine of great importance in the dye and synthetic drug industries, of m.p. 2.5° C., b.p. 193° C., and sp. gr. 0.956. (See Methylene Blue, and Malachite Green.)

**DIMETHYLBUTADIENE** — See Rubber.

**DIMETHYL FORMAMIDE** (Du Pont)  $(\text{HCON}(\text{CH}_3)_2)$  — A colourless liquid, of b.p.  $153^\circ \text{C.}$ , sp. gr. 0.954 at  $15^\circ \text{C.}$  Used as a solvent of acetylene and of synthetic resins.

**DIMETHYLGLYOXIME** (Diacetyldioxime)  $(\text{CH}_3\text{C} : \text{NOH})$  — An important reagent in the detection of nickel, said to be capable of detecting 1 part  $\text{Ni}^{++}$  in 400,000 parts of solution.

**DIMETHYL PHTHALATE**  $(\text{C}_6\text{H}_4(\text{COOCH}_3)_2)$  — A high-boiling organic solvent, sp. gr. 1.189, b.p.  $282^\circ \text{C.}$ , ref. ind. 1.514, flash point  $290^\circ \text{F.}$ , immiscible with water. It is an important plasticizer.

**DIMETHYL SULPHATE**  $((\text{CH}_3)_2\text{SO}_4)$  is a colourless liquid of sp. gr. 1.35 and b.p.  $188^\circ \text{C.}$ , with a pleasant ethereal odour, used for methylating amines and phenols in the dyestuffs and synthetic perfumes industries, and has also been used as a military poison gas. It is prepared by distillation *in vacuo* of a mixture of methyl alcohol and fuming sulphuric acid. It is very poisonous; its fumes produce violent inflammation of the larynx, bronchial tubes, and eyes, whilst the liquid blisters the skin and produces bad sores. A good methylating agent, and an important selective solvent in hydrocarbon chemistry for aromatic hydrocarbons.

**DIMETHYLTHIANTHRENE** — See Mesulphen.

**DIMORPHOUS** — See Crystals.

**DINITROBENZENES**  $(\text{C}_6\text{H}_4(\text{NO}_2)_2)$  (**Meta-** m.p.  $90^\circ \text{C.}$ , **Ortho-** m.p.  $118^\circ \text{C.}$ , and **Para-** m.p.  $173^\circ \text{C.}$ ) — Yellow crystalline intermediates, soluble in alcohol. Meta-dinitrobenzene is produced by the action of strong nitric acid on benzene, strong sulphuric acid being added to absorb the water formed during the nitration.

**DINITROCHLOROBENZENE**  $(\text{C}_6\text{H}_3(\text{NO}_2)_2\text{Cl})$  — A colourless, crystalline intermediate which in common with chloropicrin has been found capable of determining substantial crop increases, but whether by destruction of harmful organisms, increase of nitrate production, or direct stimulation of plants is not known. There are six dinitrochlorobenzenes (or better chlorodinitrobenzenes), which are made by the chlorination of dinitrobenzene or nitration of chlorobenzene.

**DINITROPHENOL** (**Alpha**)  $(\text{C}_6\text{H}_3\text{OH}(\text{NO}_2)_2(2, 4))$  — A yellow crystalline body, slightly soluble in water, soluble in alcohol and ether, of m.p.  $113^\circ \text{C.}$  Prepared by nitration of phenol. Used in the dye industry, also for making picric acid and as a fungicide for rubber. (See Explosives, and Nitration.)

**DINITROTOLUENE**  $(\text{C}_6\text{H}_3(\text{CH}_3)(\text{NO}_2)_2)$  — A yellow crystalline intermediate (2, 4; 3, 4; and 3, 5), soluble in alcohol and ether.

**DIODONE INJECTION** ("Per-Abrodil," "Pyelosil," "Uriodone") — A sterile, aqueous solution containing 35 per cent. of the diethanolamine salt of 3,5-diiodo-4-pyridone-*N*-acetic acid. Diodone is prepared by treating pyridine with thionyl chloride, hydrolysing the resulting

pyridylpyridinium chloride to form pyridone which is iodinated and treated with chloracetic acid to obtain 3,5-diiodo-4-pyridone-*N*-acetic acid and converted to the diethanolamine salt. Injection of diodone is administered by intravenous injection for the X-ray visualization of the kidneys and urinary system. Stronger solutions are sometimes employed and a 70 per cent. solution has been used for visualization of the heart by catheterization.

**DIONIN (Ethylmorphine Hydrochloride)** ( $C_{19}H_{23}O_3N.HCl.2H_2O$ ) — A white, crystalline powder, prepared by the action of diethyl sulphate on morphine in alcoholic solution and subsequent neutralization with hydrochloric acid. It is soluble in water, insoluble in ether and chloroform, and melts at about 123° C.

**DIOXAN** — See Solvents.

**DIOXIMES** — Compounds containing two oxime groups, such as benzildioxime of three forms:

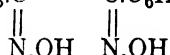
alpha- or anti-benzildioxime,  $C_6H_5.C \text{---} C.C_6H_5$ , m.p. 237° C.



beta- or syn-benzildioxime  $C_6H_5.C \text{---} C.C_6H_5$ , m.p. 206° C.  
(forms anhydride readily)



gamma- or amphi-benzildioxime  $C_6H_5.C \text{---} C.C_6H_5$ , m.p. 166° C.



**DIPENTENE (Optically Inactive Limonene)** ( $C_{10}H_{16}$ ) — A sweet-smelling terpene constituent of several modifications occurring in some essential oils, for instance citronella oil and *Oleum cinæ* (in which it is associated with lineol). It can be produced from pinene by the influence of dilute alcoholic sulphuric acid or from sylvestrene and other terpenes by several methods. Sp. gr. 0.865, b.p. 176° C.

**DIPHENAN ("Butolan," "Oxylan")** ( $C_{14}H_{13}O_2N$ ) — A colourless, odourless, crystalline compound being *p*-benzylphenylcarbamate,  $NH_2.COOC_6H_4.CH_2.C_6H_5$ ; insoluble in water; soluble in alcohol, acetone, and chloroform; m.p. 146° to 150° C. It has anthelmintic properties, and is used in medicine for the treatment of threadworm.

**DIPHENHYDRAMINE HYDROCHLORIDE** — See "Benadryl."

**DIPHENYL** ( $C_6H_5.C_6H_5$ ) — A crystalline colourless substance which can be synthesized by several methods and produced by passage of benzene vapour through a red-hot tube. It is a constituent of coal tar and readily soluble in alcohol and ether; m.p. 69° C.; b.p. 255° C.; sp. gr. 1.041. It is used in the oil industry as a vapour-phase heat-transfer medium, being non-corrosive and stable at 800° F. Its use as a starting-point in organic synthesis, including benzidine, carbazole, etc., has been described by Morgan and Walls. The commercial article is stated to be stable at from 460° C. to 482° C., with a critical temperature of about 536° C., and without action on iron and steel.

**DIPHENYLHYDANTOIN SODIUM** — See Phenytoin Sodium.

**DIPHENYLAMINE**  $((C_6H_5)_2NH)$  — A colourless, crystalline intermediate, soluble in alcohol and ether; m.p.  $53^\circ C.$ ; b.p.  $302^\circ C.$ ; prepared by heating aniline and aniline hydrochloride at from  $210^\circ$  to  $240^\circ C.$

**DIPHENYLMETHANE**  $(C_6H_5.CH_2.C_6H_5)$  is made by reaction of benzyl chloride  $(C_6H_5CH_2Cl)$  and benzene  $(C_6H_6)$  in the presence of anhydrous aluminium chloride (Friedel-Crafts reaction). It is crystalline, colourless, having a pleasant orange-like odour, soluble in alcohol and ether, and of m.p.  $27^\circ C.$ , b.p.  $262^\circ C.$

**DIPOLE MOMENT** — The dipole moment or orientation polarization of a symmetrical molecule is zero, including most hydrocarbons, carbon dioxide, carbon disulphide, 1,4-dichlorobenzene, carbon tetrachloride, silicon tetrachloride, stannic chloride, tetranitromethane, antimony pentachloride, phosphorus triiodide, oxygen, nitrogen, bromine, sulphur, and phosphorus. The dipole moment of unsymmetrical molecules is a measure of their electrical dissymmetry. The dipole moment is equal to the product of  $e$  ( $4.77 \times 10^{-10}$  e.s.u.) and the distance between the electrical centres of positive and negative charges (of the order of  $10^{-8}$  cm.). Consequently, the value of the dipole moment in all cases is of the order of  $10^{-18}$  e.s.u. The dipole moments of various liquids are shown in the accompanying table.

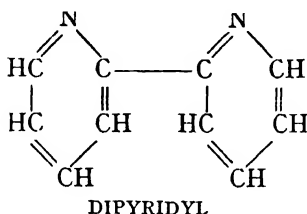
DIPOLE MOMENTS OF VARIOUS LIQUIDS AT  $20^\circ C.$

Liquid	Dipole Moment $10^{-18}$ e.s.u.	Liquid	Dipole Moment $10^{-18}$ e.s.u.
Nitrobenzene .. ..	4.2	Aniline .. ..	1.5
Nitromethane .. ..	3.4	Ammonia .. ..	1.5
Methyl nitrile .. ..	3.2	1,3-Dichlorobenzene ..	1.5
Hydrogen cyanide ..	2.9	Ethyl amine .. ..	1.3
Benzaldehyde .. ..	2.7	Ethyl ether .. ..	1.2
Acetone .. ..	2.7	Chloroform .. ..	1.1
Acetaldehyde .. ..	2.5	Hydrogen chloride ..	1.0
Glycol .. ..	2.2	Hydrogen sulphide ..	1.0
Water .. ..	1.85	Thiophene .. ..	0.6
Phenol .. ..	1.7	<i>o</i> -Xylene .. ..	0.52
Isopropyl alcohol ..	1.7	<i>m</i> -Xylene .. ..	0.46
<i>n</i> -Butyl alcohol .. ..	1.7	Toluene .. ..	0.4–0.5
Sulphur dioxide .. ..	1.6	Benzene .. ..	0.06
Ethyl alcohol .. ..	1.6	<i>p</i> -Xylene .. ..	0.06
Chlorobenzene .. ..	1.6		

See J. N. Friend's *Textbook of Physical Chemistry* (J. B. Lippincott Co., Philadelphia), vol. 2, p. 394; and P. Debye's *The Dipole Moment and Chemical Structure* (Blackie and Son, London).

**DIPPEL'S OIL (Bone Oil)** — A dark brown mixture of sp. gr. 0.910–0.970 of unpleasant odour obtained to the extent of from 5 to 10 per cent. by destructive distillation of bones from which the fat has not been previously abstracted. It contains, amongst other constituents, ammonia, ethyl benzene, pyridine, pyrrole, and is utilized as a source of pyridine and some alkaloids, whilst the pyrrole can be extracted in the form of a potassium combination ( $C_4H_4NK$ ), from which pyrrole is obtained by treatment with water. Bone oil is also used in making bone-black and as a denaturant for ethyl alcohol. (See Bone-Black.)

**DIPYRIDYL** — A diamine produced by dehydrogenating pyridine with dry ferric chloride under pressure at  $200^\circ C$ . A reagent used for the detection of ferrous iron. The reaction is sufficiently delicate to detect



3 parts of ferrous in 10,000,000 parts of solution. Ferric iron and organic matter do not interfere with the reaction. Co-ordination compounds are formed with ferrous salts, with nickel salts, and with ethylene diamine.

**"DISCOL"** — A motor fuel of alcoholic character made from molasses.

**DISINFECTANT** — A substance which has the power of killing bacteria and micro-organisms. Many different types of chemical compounds are used as disinfectants including phenols (phenol, cresol, and resorcinol), chlorinated phenols (chlorocresol, chloroxylenol), hypochlorites (Dakin's solution), oxidizing agents (hydrogen peroxide, potassium permanganate), mercury compounds, and many other substances, including many dyestuffs.

Whilst chemical tests can be applied to determine the purity of substances used as disinfectants, the antibacterial activity can only be assessed by microbiological methods. This is usually done by comparing the activity with that of phenol against a standard strain of a test organism cultivated under standard conditions. This forms the basis of the Rideal-Walker Test which is subject to definite limitations and has been modified considerably to increase its usefulness and accuracy. For a critical review and extensive bibliography of methods of testing the efficiency of disinfectants, see "The Evaluation of Germicides for Commercial and Clinical Purposes," by I. Michaels (*Mfg. Chemist*, 19, 5, 60, 109 (1948).) (See Antiseptics, Bacteria, Bactericides, Dyes, and Seed Disinfectants.)

**DISINTEGRATION** — The process of spontaneous nuclear change in which an alpha or beta particle is emitted. After such a process the nucleus has a different atomic number from its original one.

**DISINTEGRATORS** — Machines for grinding, granulating, or shredding materials. (See Crushing.)

**DISPERSION** — (1) A term used in connection with colloid chemistry. (See Colloid Chemistry.) (2) The separation of light into its different coloured rays. (See Light and Wave Lengths.)

**DISPERSOIDS** — See Colloid Chemistry, and Osmosis.

**DISSOCIATION** — Spontaneous or forced acts of decomposition. For example, when ammonium chloride is heated sufficiently, it is decomposed into ammonia and hydrogen chloride gases, which recombine upon cooling in the presence of each other. The dissociation pressure of the resultant gases is a function of the temperature. Ammonium chloride sublimes if heated at one portion of a glass tube and the more distant portion is not heated. Dissociation of solids, liquids, and gases is accompanied by the absorption of heat. Further examples:  $\text{H}_2\text{SO}_4 + \text{Heat} \rightleftharpoons \text{H}_2\text{O} + \text{SO}_3$ ;  $\text{SO}_3 + \text{Heat} \rightleftharpoons \text{SO}_2 + \frac{1}{2}\text{O}_2$ ;  $\text{CaCO}_3 + \text{Heat} \rightleftharpoons \text{CaO} + \text{CO}_2$ ;  $2\text{NH}_3 + \text{Heat} \rightleftharpoons \text{N}_2 + 3\text{H}_2$ ;  $\text{Pb}_3\text{O}_4 + \text{Heat} \rightleftharpoons 3\text{PbO} + \frac{1}{2}\text{O}_2$ ;  $\text{CO}_2 + \text{Heat} \rightleftharpoons \text{CO} + \frac{1}{2}\text{O}_2$  (at 1,230° C., 1.0 atm., 0.041%  $\text{CO}_2$  dissociated; at 1,730° C., 1.0 atm., 1.77%  $\text{CO}_2$  dissociated);  $\text{H}_2\text{O} + \text{Heat} \rightleftharpoons \text{H}_2 + \frac{1}{2}\text{O}_2$  (at 1,230° C., 1.0 atm., 0.022%  $\text{H}_2\text{O}$  dissociated; at 1,730° C., 1.0 atm., 0.59%  $\text{H}_2\text{O}$  dissociated).

Electrolytic dissociation is referred to under Electricity (Electrochemical Aspects).

“ **DISSOLVED ACETYLENE** ” — See Acetylene.

**DISSYMMETRY** — See Asymmetry, and Crystals.

**DISTEMPERS** — See Paints.

**DISTILLATION** — A method of separating the components of liquid mixtures, or mixtures of liquids and solids, by heating them and condensing the vapours. “ Destructive distillation ” is a term sometimes applied to the decomposition of wood, coal, and other non-volatile materials by heat to yield liquid products. In this process, which is properly termed Pyrolysis, the original substances are chemically changed, while in true distillation there is no chemical change.

The ease with which any two substances may be separated by distillation is measured by the Relative Volatility of the more volatile substance A with respect to the less volatile substance B, which is defined as the ratio of A to B in the vapour phase divided by their ratio in the liquid phase when a mixture of the two substances is vaporized under equilibrium conditions. In general, relative volatility tends to decrease as temperature increases. Hence as a rule separations are somewhat more easily accomplished at lower temperatures, *e.g.*, by distillation under vacuum. At any given temperature :

$$\alpha = \frac{f_A}{f_B} = \frac{\gamma_A P_A}{\gamma_B P_B} = \frac{K_A}{K_B}$$

where  $\alpha$  = relative volatility of component A with respect to B,  $f$  = fugacity,  $\gamma$  = activity coefficient,  $P$  = vapour pressure,  $K$  = **Equilibrium Ratio** (*q.v.*). For mixtures which obey Raoult's, Dalton's, and

the Gas laws, activity coefficients are unity and  $\alpha = P_A/P_B$ . In certain mixtures, known as Azeotropes, the activity coefficients of the components are such that the relative volatility is unity. Such mixtures cannot be separated by ordinary distillation. Ethyl and some higher alcohols form azeotropes with water; methyl alcohol does not.

Distillation may be either simple or fractional. Either process may be carried out in batches, semi-continuously or continuously, and at various pressures.

In **Simple Distillation**, the vapour rising from the boiling liquid is condensed directly, and no reflux is returned to the still. The latter consists essentially of a flask or kettle which can be heated, connected by a vapour pipe to a condenser and distillate or condensate receiver. The principles of batch and continuous operation need no explaining. Semi-continuous distillation is sometimes used where the percentage of residue is small. The kettle is charged and heated as in batch distillation, but in addition, as the operation proceeds, a continuous stream of charge is admitted to replace the material vaporized until enough residue has accumulated to fill the kettle. The operation is then discontinued.

Substances that decompose below their atmospheric boiling points may be distilled at reduced pressure or in a current of steam. Substances that are normally gaseous may be distilled under pressures high enough to liquefy them, but the temperature of distillation must be below the critical temperatures of the substances.

When simple distillation is applied to a mixture of volatile liquids, the distillate is richer in the more volatile components, and the residue is richer in the less volatile components, but all components are present in both distillate and residue. Simple distillation cannot effect a sharp separation unless one component is substantially non-volatile (as in the purification of water from dissolved solids by distillation), or unless the relative volatility of the lighter component is extremely high with respect to the other (as in the recovery of gasoline from used crankcase lubricating oil).

The composition of the residue and distillate from a simple distillation may be calculated from Rayleigh's equation if the relative volatilities are known.

Let  $A_1, B_1, C_1 \dots$  Total mols of components A, B, C, in the original mixture.

$A_2, B_2, C_2 \dots$  Total mols of components in the residue after distillation.

$\alpha, \beta, \dots$  Average relative volatilities (over the temperature range of distillation) of component A vs. B, B vs. C, etc.

Then  $\log_e \frac{A_1}{A_2} = \alpha \log_e \frac{B_1}{B_2}$ ;  $\log_e \frac{B_1}{B_2} = \beta \log_e \frac{C_1}{C_2}$ ; . . . etc.

Knowing the total mols of residue, one can calculate the mols of each component in it, and, by difference, obtain the composition of the distillate.

In **Fractional Distillation**, a fractionating column is superimposed upon the kettle, and the vapour passes upwards through it before reaching the condenser. A portion of the condensate is returned as reflux to the top of the column where, descending against the rising current of vapour, it absorbs heavy components and is progressively denuded of light components until it reaches the kettle. By increasing the height of the column and the proportion of reflux, one can make the separation of any two components as complete as desired, provided that there is some difference in volatility.

Fractionating columns are of two kinds, packed columns and plate columns. The former are plain vertical tubes filled with beads, rings, or other loose bodies providing a permeable mass through which the vapour can rise and an extended surface for interaction between vapour and reflux. For efficient fractionation, the diameter of the loose packing bodies should not exceed one-eighth of the inside diameter of the column. Packed columns are used in the laboratory and for the smaller kinds of industrial columns. In larger sizes they tend to develop an uneven distribution of reflux over the cross-section of the packing, and plate columns are then more satisfactory.

A plate column contains a succession of carefully levelled horizontal plates at each of which vapour and reflux are brought into intimate contact. The plates may be simple perforated discs, or they may be bubble trays with elaborate provision for bubbling the vapour through a layer of liquid reflux. In bubble-tray columns the reflux is usually caused to flow across each tray and through a liquid-sealed downspout to the tray below.

Fractional distillation may also be carried out either batchwise, semi-continuously or continuously, under vacuum or with steam. In continuous operation the charge is introduced part-way up the column, the lower section of which then acts as a stripping column, while the upper section serves to concentrate the lighter components.

**Azeotropic Distillation** is a method of separating two components of equal volatility by adding a third substance which forms an azeotrope with one of the components. The azeotrope usually boils at a lower temperature than the components alone, and it can thus be distilled off through a fractionating column.

There is an immense literature on the theory of distillation and methods of determining the number of plates (or height of packing) and the reflux ratio required to effect a given separation. The most rigorous methods involve the stepwise computation of liquid and vapour compositions from plate to plate by means of heat balances, material balances, and vapour-liquid equilibrium data, the equations being solved either analytically or graphically. Less rigorous methods dispense with heat balances. Even so, when more than two components are present the calculations become very tedious, necessitating trial-and-error solution at every plate. A useful short cut for sumating purposes is provided by the empirical correlations of Brown and Martin (*Trans. Am. Inst. Chem. Engrs.*, **35**, 679 (1939)) and Gilli- (1949)). *Chem.*, **32**, 1220 (1940)). These approximations are

based on the minimum reflux ratio and minimum number of theoretical plates, both of which can be calculated fairly easily. The simplest method of calculating the minimum reflux ratio for multi-component mixture is described in *J. Inst. Petroleum*, **32**, 598, 614 (1946), and *Chem. Eng. Progress*, **44**, 603 (1948).

*References*: Standard works listed under Chemical Engineering; S. Young, *Distillation Principles and Processes* (Macmillan, London); Robinson and Gilliland, *Elements of Fractional Distillation* (McGraw-Hill Book Co., New York); A. J. V. Underwood (*Trans. Inst. Chem. Engrs.* (London), **10**, 112 (1932)); Emil Kirschbaum, *Distillation and Rectification* (Chemical Publishing Co., Brooklyn); also numerous papers in *Ind. Eng. Chem.*, *Trans. Am. Inst. Chem. Engrs.*, and *Chem. Eng. Progress*.

“**DITHANE**” — Disodium ethylene bisdithiocarbamate, used as a fungicide.

**DITHRANOL** (“**Derobin**”) ( $C_{14}H_{10}O_3$ ) — A yellow, odourless, and tasteless powder, namely, 4,5-dihydroxyanthranol ( $C_{14}H_7(OH)_3$ ); insoluble in water; slightly soluble in alcohol and ether; soluble in chloroform and fixed oils; m.p.  $174^\circ$  to  $178^\circ$  C. It is used, in the form of an ointment, for the treatment of psoriasis and other skin conditions. (See Chrysarobin.)

**DIVALENT** — See Valencies.

**DIVINYL OXIDE** — See Ethers (Vinyl).

**DIVI-DIVI** — The dried seed pods of *Cesalpinia coriaria*, indigenous in tropical America, of growing importance in the tanning industry; capable of yielding as much as 300 lbs. of pods per season, and containing a very astringent tannin ranging from 40 to 45 per cent. Venezuela is the most important source, and the Goajira Peninsula of Colombia ranks next.

“**D.O.C.A.**” — See Deoxycortone Acetate.

**DOCTOR TEST** — A test that is applied to petroleum distillates and indicates the presence or absence of hydrogen sulphide and organic sulphides. A solution of sodium plumbite prepared by dissolving litharge in sodium hydroxide is added to the oil to be tested, along with flowers of sulphur, and the whole is shaken. A dark coloration is a positive test.

**DOLOMITE** — A rock consisting of varying proportions of calcium and magnesium carbonates, of crystal system No. 3, and sp. gr. 2.8 to 2.9. It occurs throughout much of the earth. Upon calcining, it finds extensive use as basic (contrast to acidic silica) refractory brick, and as raw material for the extraction of magnesium. Sodium silicate solution and dextrin-water mixtures give good results as binding agents for dolomite. (See Magnesium, and Refractories.)

**DOPES** — Various solutions or varnishes used in the aeroplane and cinema industries, etc., made by dissolving cellulose or cellulose compounds in certain solvents, including acetone; amyl alcohol; anisyl,

butyl, and ethyl acetates; dichloro and trichlorethylene, tetrachlorethylene (perchlorethylene), tetrachlorethane, and pentachlorethane. A small proportion of boric acid is sometimes added to cellulose dopes in order that they may retain their viscosity. It has been stated that 5 to 8 per cent. of ammonium phosphate or ammonium magnesium phosphate added to cellulose nitrate renders it fire-resistant, and qualifies it to compete with cellulose acetate as an aeroplane dope.

See G. M. Kline on "Fire-Resistant Doped Fabric for Aircraft" (*Ind. Eng. Chem.*, **27**, 556, (1935)); F. Sproxton, *Cellulose Ester Varnishes* (E. Benn, London); Cellulose Solvents, Films, Lacquers, and Viscose.

**DOPPLERITE** — A peculiar brownish-black, jelly-like material found infrequently at some distance below the surface of peat-bogs, being a colloidal body belonging to the so-called ulmin compounds resulting from the decay of vegetable matter. Two published analyses are as follows:

				Dull	Brilliant
Carbon .. ..	..	..	..	57.90	56.70
Hydrogen .. ..	..	..	..	5.31	4.92
Oxygen .. ..	..	..	..	34.00	36.60
Nitrogen .. ..	..	..	..	2.10	1.10
Sulphur .. ..	..	..	..	0.70	0.70

Upon drying it acquires a hard, shiny appearance similar to that of the vitrain of banded bituminous coal. (See Coal, and Peat.)

"**DORSITE**" — An activated carbon. (See Carbon (Activated)).

"**DORYL**" — See Carbachol.

"**DOUCIL**" — A proprietary, compound aluminosilicate water-softening material of the base-exchanging character, and admitting of regeneration by treatment with a solution of common salt. Its approximate composition is  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 5\text{SiO}_2$ . (See Ion Exchange, and Water Conditioning.)

**DOVER'S POWDER** — A powder containing opium and ipecacuanha, used in medicine as a sedative and diaphoretic. It contains 1.0 per cent. morphine.

"**DOWMETAL**" — Various alloys of magnesium with small amounts of other metals, used principally in the construction of aeroplanes and other industrial applications where light weight and structural integrity are prime factors. (See "Elektron Metal.")

**DRAGON'S BLOOD** — See Balsams, and Gums and Resins.

"**DRAMAMINE**" ( $\text{C}_{24}\text{H}_{30}\text{O}_3\text{N}_5\text{Cl}$ ) — An organic compound, namely  $\beta$ -dimethylaminoethyl benzohydryl ether 8-chlorotheophyllinate, prepared by dissolving 8-chlorotheophyllin with an excess of the base in hot ethylmethyl ketone or ethyl alcohol and cooling (see *Science*, **109**, 547 (1949)). "Dramamine" has been used for the prevention of sea and K.C.E.—11

air sickness (see B. A. Strickland and G. L. Hahn, *Science*, **109**, 359 (1949); and L. N. Gay and P. E. Carliner, *Science*, **109**, 359 (1949)).  $\beta$ -Dimethylaminoethyl benzohydryl ether is itself one of the anti-histamine group of drugs (see “Benadryl”).

“**DRIERITE**”—Anhydrous calcium sulphate, for removing moisture from liquids and gases. As it is insoluble in organic liquids, it does not swell or cake upon absorbing moisture, and it can be readily regenerated. By the addition of a moisture-sensitive colour, such as anhydrous cobalt chloride, the progress of its hydration can be observed.

**DRIERS**—See Oils, Siccatives, and Varnishes.

**DROP BLACK**—Residual bone-black from the sugar-refining industry, washed and ground for use in the paint and enamel trades.

**DRY CLEANING**—The process of removal of grease and stains from clothing and fabrics by the use of a solvent, such as cleaner’s naphtha, benzene, carbon tetrachloride. Chlorinated hydrocarbons are very satisfactory as dry-cleaning solvents, but possess the disadvantage of toxicity, which factor must be balanced against that of inflammability in the case of petroleum and coal-tar hydrocarbons.

**DRY ICE**—See Carbon Oxides (Carbon Dioxide).

**DRYING**—Drying of solids can be effected to a considerable extent by pressure, and there are well-understood methods of drying applicable to liquids and gases. So-termed “spray drying” is carried out by means of a spraying device which carries the finely divided substance into a chamber in which it encounters a current of hot air, causing evaporation and deposition of the dry product in the chamber. Any escaping powder carried away by the current of air is recovered by filters. There are two types of spraying devices, one of which acts by stationary nozzles and the other by means of centrifugal force. In film drying the liquid is passed over the heating surface in the form of a thin film.

Drying of gases is necessary in full air-conditioning and for many catalytic processes. Moisture may be removed by concentrated sulphuric acid, by calcium chloride, or by activated alumina or silica. The relative humidities of several drying agents at 20° and 60° C. are presented in tabular form. See J. H. Perry and H. C. Duus on “Drying Gases by Absorption” (*Chemical and Metallurgical Engineering*, **41**, 74 (1934)).

In chemistry and chemical engineering the term “drying” is used in various senses, *e.g.*, (1) the removal of absorbed or adhering water from solid substances by evaporation, (2) the rapid evaporation of solutions to yield a solid, dry residue (*e.g.*, spray drying), (3) the removal of water vapour from gases, (4) the removal of dissolved or entrained water from non-aqueous liquids. In (3) the desired result can be accomplished by treating the gas with a solid or liquid dehydrating reagent, or with a solid adsorbent, and in (4) by settling, distillation, extraction, or adsorption. (See Absorption, Adsorption, Distillation, and Extraction.) The following discussion deals with drying in (1) and (2) only.

(1) When a very wet solid is exposed to a current of air or other gas, the rate of drying is at first independent of the water content of the solid, and depends only on the velocity, temperature, and humidity of the air (or gas) current. When the water content of the solid has

SOME SOLID DRYING AGENTS AND THEIR RELATIVE HUMIDITIES

At 20° C.		At 60° C.	
Solid	Relative Humidity Per cent.	Solid	Relative Humidity Per cent.
LiCl.H <sub>2</sub> O .. ..	15	MgSO <sub>4</sub> .6H <sub>2</sub> O .. ..	82
CaCl <sub>2</sub> .6H <sub>2</sub> O .. ..	32	CuCl <sub>2</sub> .2H <sub>2</sub> O .. ..	84
Zn(NO <sub>3</sub> ) <sub>2</sub> .6H <sub>2</sub> O .. ..	42	CuSO <sub>4</sub> .5H <sub>2</sub> O .. ..	95
Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> .2H <sub>2</sub> O .. ..	52		
Mg(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>2</sub> .4H <sub>2</sub> O .. ..	65		
NaC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> .3H <sub>2</sub> O .. ..	76		
KHSO <sub>4</sub> .. ..	86		
ZnSO <sub>4</sub> .7H <sub>2</sub> O .. ..	90		
Na <sub>2</sub> SO <sub>4</sub> .10H <sub>2</sub> O .. ..	93		

SOME DRYING AGENTS AND THEIR ABSOLUTE DRYING POWER

Drying Agent	Absolute Drying Power
P <sub>2</sub> O <sub>5</sub> .. ..	Much less than 1 mg. of H <sub>2</sub> O in 40,000 litres of gas
Mg(ClO <sub>4</sub> ) <sub>2</sub> , anhydrous ..	Unweighable amount of H <sub>2</sub> O in 210 litres of gas
KOH, fused .. ..	0.002 mg. of H <sub>2</sub> O in 1 litre of gas
H <sub>2</sub> SO <sub>4</sub> .. ..	0.003 mg. of H <sub>2</sub> O in 1 litre of gas
NaOH, fused .. ..	0.16 mg. of H <sub>2</sub> O in 1 litre of gas
CaO .. ..	0.2 mg. of H <sub>2</sub> O in 1 litre of gas
CaCl <sub>2</sub> , granular .. ..	0.14-0.25 mg. of H <sub>2</sub> O in 1 litre of gas
CaCl <sub>2</sub> , fused .. ..	0.36 mg. of H <sub>2</sub> O in 1 litre of gas
Al <sub>2</sub> O <sub>3</sub> .. ..	0.003 mg. of H <sub>2</sub> O in 1 litre of gas
CaSO <sub>4</sub> .. ..	0.004 mg. of H <sub>2</sub> O in 1 litre of gas
MgO .. ..	0.008 mg. of H <sub>2</sub> O in 1 litre of gas
ZnCl <sub>2</sub> .. ..	0.8 mg. of H <sub>2</sub> O in 1 litre of gas
CuSO <sub>4</sub> .. ..	1.4 mg. of H <sub>2</sub> O in 1 litre of gas

fallen to a certain value, termed the Critical Water Content, the drying rate thereafter decreases as a function of the residual water content. The first stage is called the constant rate period, and the second, the falling rate period. (It would constitute a useful distinction if solids having a water content above the critical value were generally classified as "wet." and those having less than the critical content, as "damp.")

During the constant rate period the drying rate is controlled by the rate of diffusion of water vapour from the surface of the solid through the laminar film of air above it (see Fluid Dynamics). During the falling rate period the drying rate is also affected by the rate of liquid diffusion from the interior of the solid to the surface.

The rate of drying of flat surfaces during the constant rate period, for air flow parallel to the surface, is approximately given by the equation:  $W = 0.021G^{0.8}(p_s - p_a)$ , where  $W$  = pounds of water evaporated per square foot of surface per hour,  $G$  = mass velocity of air in pounds per square foot of air cross-section per second,  $p_s$  and  $p_a$  = partial pressure of water vapour in mm. of mercury at the solid surface temperature and in the air stream respectively. When the solid surface is at the wet-bulb temperature, *i.e.*, when no heat is supplied to the solid,  $(p_s - p_a)$  is about equal to one-half the wet-bulb depression in degrees C. For the falling rate period, more complex relationships hold.

Industrial dryers for solids are classified as intermittent or continuous, and as adiabatic or isothermal. In adiabatic dryers, all the heat required for evaporation is supplied by the incoming air. The temperature along the dryer therefore falls as the moisture content of the air increases. Isothermal dryers are internally heated so that the air temperature is kept approximately constant. Adiabatic dryers are the simpler and cheaper, but isothermal dryers are better for drying materials that are sensitive to high temperature.

Intermittent adiabatic dryers include loft and chamber dryers of various kinds in which the material to be dried is stacked in closed compartments through which air or gases are caused to circulate. The drying air may be heated by steam coils, or hot combustion gases may be introduced into the chamber. Tunnel dryers are similar in principle, but semi-continuous. The wet material is loaded on trucks and placed in a tunnel furnished with rails and closed at both ends. Periodically a truck of dry material is removed from one end of the tunnel and a truck of fresh material introduced at the other end. The air or gases pass through the tunnel countercurrent to the material. Tunnel dryers may be either adiabatic or isothermal; in the latter case steam coils are provided inside the tunnel.

The rotary dryer is a continuous adiabatic dryer adapted for dealing with granular or coarsely powdered material. It consists of a hollow rotating cylinder inclined at a slight angle to the horizontal and provided with internal lifting plates. Hot air or gases pass through the dryer countercurrent to the material, which is continually raised by the lifting plates as the cylinder rotates and allowed to fall through the gas stream.

Continuous screen dryers have a vibrating screen across which the material to be dried is caused to move, and through which a current of hot air is passed. The material must be relatively coarse and free-flowing.

Vacuum tray dryers are used for the batch drying of temperature-sensitive materials. They operate on the isothermal principle, and

consist of a closed chamber containing shelves heated by hot water or steam. The wet material is spread on the hot shelves and the chamber is closed and evacuated.

A dryer which is neither adiabatic nor isothermal is the intermittent agitator dryer, sometimes used for drying small batches of solids. It consists of an open pan or trough heated externally and provided with revolving paddles to keep the material in motion. Such a dryer may also be provided with a cover and operated under vacuum. Heat transfer in the agitator dryer is poor, and it is unsuitable for materials which tend to cake on hot metallic surfaces.

For dryer calculations a humidity chart is needed. The most convenient form is the Grosvenor chart, in which atmospheric humidity is expressed as pounds of water per pound of dry air. Such charts are given in standard chemical engineering works.

(2) The principal types of dryers for liquids are spray dryers and drum dryers. In a spray dryer the preheated liquid is sprayed in small droplets into a large chamber concurrently with a stream of heated air. Atomization may be effected by either a pressure nozzle, an air-atomizing nozzle, or a spinning disc or cup. The last method is said to give the most uniform particle size. Some of the dried product collects as a powder on the floor of the drying chamber; the rest passes out with the air stream and is recovered in a cyclone.

Drum dryers have one or more revolving metal cylinders heated internally with steam. A thin film of liquid is supplied to the cylinder surfaces, and the dried product is removed by stationary scrapers, the vapours being carried off by a fan. Drum dryers produce a flaky product, as compared with the spherical particles obtained from a spray dryer. Of the two, the drum dryer has the higher thermal efficiency. It may also be adapted to operate under vacuum.

*References:* Standard works listed under Chemical Engineering.

**DRYING OILS** — See Oils, and Linseed Oil.

**DRYING TUBES** — Appliances used for drying gases, some being straight or other shaped tubes packed with small lumps of calcium chloride or other substance that has a great affinity for moisture. The increase in the weight of the tube gives the weight of the water absorbed, from which may be calculated the proportion of hydrogen contained in a known weight of an organic substance when the same has been burned in a current of dry oxygen. (See Organic Analyses.)

**DRY ROT** — See Wood.

**"DUCO"** (Du Pont) — Trade-mark for a series of lacquers, enamels, and undercoats. Used specially in the automotive and furniture trades.

**DUCTILE** — Easily drawn into wire. (See Metals.)

**DUGONG OIL** — See Fish Oils.

**DULCITOL (Dulcin, Dulcite)** ( $C_6H_8(OH)_6$ ) — A white, sweet, crystalline, saccharine body, obtained from the dried herb *Melampyrum memorosum* at the flowering time, and the red seaweed *Bostrychia scorpioides* (Haas and Hill); soluble in water and isomeric with mannite (mannitol), both being hexahydric alcohols. (See Galactose.)

**DULONG AND PETIT'S LAW** — See Heat.

“**DULUX**” (Du Pont) — Trade-mark for synthetic resins. Used specially for air-drying and baking varnishes and enamels.

“**DUPONOL**” (Du Pont) — Trade-mark for a series of fatty alcohol sulphates. Used as scouring and emulsifying agents, and as detergent, dispersing, and wetting agents in the cosmetic, textile, and leather industries.

“**DUPRENE**” — Name of a synthetic chloro-rubber. Probably the same as chloroprene (see Acetylene Industries, Chart II).

“**DURALUMIN**” — An alloy, sp. gr. 2.85, containing more than 90 per cent. aluminium, 0.5 per cent. magnesium, and some proportions of copper, iron, and manganese (3.0 to 4.5 per cent. Cu ; 0.4 to 1 per cent. Mg ; 0 to 0.7 per cent. Mn ; and remainder commercial aluminium containing iron and silicon). The age-hardening of alloys of this type is said to be primarily due to the magnesium silicide ( $Mg_2Si$ ) content.

**DURANTHRENE COLOURS** — Derivatives of anthraquinone, being vat colours of excellent fastness, suitable for dyeing vegetable fibres in all stages of manufacture.

**DURENE** (1, 2, 4, 5-Tetramethylbenzene) ( $C_6H_2(CH_3)_4$ ) is a colourless crystalline body of m.p. about  $80^\circ C.$ , and b.p. about  $194^\circ C.$ , occurring in coal tar. It has a camphoraceous odour, and can be made from toluene or xylene by several processes.

“**DURIMET**” — An American acid-resisting metal, being steel of several grades containing proportions of nickel, silicon, chromium, and carbon.

“**DURIRON**” — An American acid-resisting metal, containing about 14 per cent. silicon and small proportions of manganese, carbon, phosphorus, and sulphur.

“**DUROGLASS**” — Trade name for borosilicate chemical-resistance glassware of high thermal endurance.

“**DUROPRENE**” — A proprietary article (heptachloride of rubber), prepared by the combined action of bromine and chlorine on rubber and used in compounding paints or varnish for the prevention of rust on metals, etc. It is a greyish-white powder, soluble in benzol, naphtha, and carbon tetrachloride, and easily moulded when warmed.

“**DUROSIL**” — Trade-name for a chemical glass, free from lead, arsenic, and antimony.

**DUSTS AND DUST EXPLOSIONS** — Investigations made by the U.S.A. Bureau of Mines have shown that—

1. 0.2 ounce coal dust per cubic foot of air will propagate an explosion.

2. Using a long flame explosive of black powder or dynamite may cause ignition of a coal-dust cloud.

3. Dust-laden air will explode when either quiescent or moving near the lighting flame, even when saturated with moisture, provided enough dust be present in the air.

Dust explosions are not confined to coal, but extend to atmospheric mixtures of many other ignitable substances, such as starch, meal, flour, cake refuse, sugar, etc., if the proportions of dust and air lie (as in the case of gas) within certain limits.

It is stated that dust particles which float in the air cannot be much larger than 0.001 cm. diameter, "smokes" being defined as systems in which the solid particles exhibit Brownian movement when dispersed in a gas. (See Colloidal State.)

Precipitated calcium carbonate has been advocated by A. C. Dunningham as approximating most nearly to the ideal substance for stone dusting of mines and as preferable to shale dust.

Dust removal from gases is referred to under the heading of "Cottrell Precipitating Plant." As to dust explosion risks, see R. V. Wheeler (*Chem. and Ind.*, **50**, 650 (1931)); *Safety in Mines Research Board Paper*, No. 48 (H.M. Stationery Office); *Memorandum on Dust Explosions*, compiled by Factory Department of the Home Office (H.M. Stationery Office); various publications of the U.S. Bureau of Mines; *The Dust Hazard in Industry*, by W. E. Gibbs (E. Benn, Ltd., London); see also Coal, Mists, and Particles.

**DUTCH LIQUID** — See Ethylene Dichloride.

**DUTCH METAL** — An alloy of 11 parts of copper and 2 parts of zinc prepared in leaf form in imitation of gold leaf.

**DUTCH WHITE** — White Lead.

**DVI** — Prefix being the Sanskrit numeral two.

**DYADS** — See Valencies.

**DYER'S BROOM** (*Genesta tinctoria*) — Found in pastures and thickets in Southern Europe, Russian Asia, Southern Sweden, and some parts of Great Britain and North America. It contains two principles, one of which is a yellow colouring matter of crystalline character and another named genistein ( $C_{14}H_{10}O_6$ ), which can be obtained in the form of colourless crystals.

**DYES AND DYEING** — There are thousands of dyes, in addition to mineral pigments, some being natural products, such as cochineal, barwood, brazil-wood, madder, indigo, logwood, peach-wood, cutch, gambier, fustic, sumac, annatto, and safflower, of which descriptions will be found under their respective names; but for the most part they are chemically (synthetically) produced substances from coal-tar sources, natural dyes having been almost entirely displaced by synthetic dyes.

**Classes of Dyes** — The U.S. Tariff Commission compiles, since 1917, an annual census of production of dyes, and, since 1921, of other synthetic organic chemicals, under the title of *Synthetic Organic Chemicals*. Four classes of dyes accounted for about 85 per cent. of the total dye production in 1945, namely, azo (39 per cent.) and anthraquinone (22 per cent.) vat dyes, the sulphur or sulphide (12 per cent.) dyes, and the idigo and thioindigo (12 per cent.) dyes. Statistics for 110,000,000 pounds of individual dyes valued at \$70,000,000 are given in the report.

**Dyeing** — The manner in which dyes become attached to the fabrics varies according both to the chemical constitution of the fabrics themselves and those of the dyes employed. In some cases, definite compounds are formed by the action of the dyes on the fabrics; in other cases, "lakes" are formed by the agency of mordants, the precipitated substances being thus directly attached to the fabrics; and in yet other cases the dyes are developed on the fibres. Basic dyes (salts of colourless bases) containing amino groups, including mauve, magenta, methylene blue, malachite green, and Bismarck brown, are fixed on cotton goods by the use of acidic mordants. Acidic dyes, including picric acid, azo-scarlets, and aniline blue, are attached to wool and silk goods by the use of an acid-bath. Some acidic dyes, such as alizarin red and others in the form of sodium salts of the sulphonic acids, require the use of a metallic mordant. Dyes of a saline nature, like the Congo-red and primulin series, are used for cotton and linen without any mordant, and there are pigment dyes, such as chrome yellow, synthetic indigo, and aniline black, in respect of which the colour is developed on the fibres.

The dyestuffs are also classed as "substantive" and "adjective," the former having the property of dyeing fibres directly, while the latter only colour them permanently when used in association with mordants.

Vat dyestuffs comprise a series of insoluble bodies admitting of reduction to alkali-soluble leuco (colourless) compounds, many being derivatives of anthracene. They are applied in their leuco compounds, the colour in the fibre being subsequently developed by oxidation, and include notably methane derivatives of triphenylmethane dyestuffs. The anthraquinoid vat colours are of particular value in cotton dyeing owing to their fastness to light and washing. The best-known indigoid vat dyestuff is indigo itself. In wool-dyeing the insoluble dyestuffs are now almost invariably rendered soluble by use of hydrosulphites, which reduce them to leuco compounds. Many of the azo dyes dye cotton without the use of a mordant, while others act as very fast dyes on wool. They may be regarded as originating from the red crystalline parent substance azobenzene ( $C_6H_5.N : N.C_6H_5$ ) or its homologues, all its basic and acid derivatives being colouring matters. The basic ones contain  $NH_2$  or  $N(CH_3)_2$  groups and the acidic ones either phenolic (OH) or sulphonic ( $SO_2.OH$ ) and phenolic groups.

Group compounds containing such as  $-N : N-$  or  $NO_2$  are known as chromophores and produce dyes when introduced into so-called chromogens—that is, compounds which contain unsaturated groups of  $C_6$  arranged as in benzene. (See Chromogens, and Chromophores.)

The sulphur group, produced by the fusion of amino aromatic compounds with sulphur or by heating a variety of organic bodies with sulphur and sodium sulphide, are of more or less unknown constitution. They include the "Indo-Carbon C.L.," and many are made from dinitrophenol ( $C_6H_3(NO_2)_2OH$ ), "sulphur black" being made from it by action of sodium sulphide and sulphur.

Black and dark-coloured dyestuffs are also produced by condensing amino derivatives with highly halogenated vat dyestuffs followed, if desired, with further ring closure.

The so-called "ciba" and "cibanone" vat dyes are indigo derivatives containing bromine.

Previous to dyeing, cotton and wool are subjected to purifying and bleaching treatment. (See Bleaching.)

**Mordants** — Wool absorbs colours and mordants much more readily than cotton, while silk can be dyed with coal-tar colours by mere immersion in an aqueous or alcoholic solution. As a rule, cotton goods will not dye without previous treatment with a mordant, the mordant in such cases directly combining with, and thus fixing, the dye and the mordants used; for acid dyes, feeble bases like aluminic, chromic, and ferric hydroxides (which are produced on the fabrics by immersing them in solutions of the acetates of these bases and steaming them) are used, the colours of the "lakes" so produced varying with the base employed. Using basic dyes for cotton goods, these are first mordanted with tannic acid or a tin salt, such as the chloride.

**Fastness** to washing and light is obtained in some cases by the action of metals—copper and chromium salt solutions, for example,—on the colours. The atmospheric fading of dyestuffs is not exclusively due to the action of light. Humidity, temperature, the chemical character of the atmosphere, perspiration, and other factors exercise influences. Ultra-violet rays of very short wave-length are very destructive to colours of dyes.

**Special dyes** and a special treatment are required for dyeing cellulose acetate fibres. Such dyes as aminoazobenzene and 1,4-diaminoanthraquinone are used, and dispersed into the colloidal state by soaps or sulphated fatty alcohols.

Certain insoluble azo-compounds are dispersed by blending with a soluble oil such as sulphonated ricinoleic acid and accordingly then dispersed dyes are termed S.R.A. colours. Dispersed colours are similar preparations made up with other distributing agents. The Duranol dyes, sold as pastes or as redispersible powders, contain in the main such as anthraquinone derivatives as 1-aminoanthraquinone (yellow) 1,4-diaminoanthraquinone (violet) and diaminoanthrarufin (blue). These dyes, which furnish dark shades, are in such a high state of dispersion that they may be applied by a simple one-bath process. The Solacet colours, although soluble in water, dye acetate silk in full shades just as direct dyes are applied to cotton and other cellulose fibres. Certain Solacet dyes are monazo-compounds in which various benzenoid and naphthalenoid diazonium salts are coupled with reactive aromatic tertiary amines containing a lengthy side chain such as  $-\text{CH}_2\cdot\text{CH}_2(\text{O}\cdot\text{CH}_2\cdot\text{CH}_2)_n\cdot\text{OH}$ . The earliest dyes for cellulose acetate were the Ionamines such as Ionamine B  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{SO}_3\text{Na}$ , which gives an orange shade  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$  developable by diazotization and coupling with  $\beta$ -naphthol to produce a scarlet shade  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ .

Furs have to be dressed by a tannage treatment before dyeing, and

after "wetting out" they are "killed" by steeping in or brushing with a dilute alkaline solution such as ammonia, soda, or lime, this being done to kill the resistance exhibited by the hair to the action of the dye. They are then mordanted by steeping in some solution of a metallic salt such as copper sulphate, sodium dichromate, alum, iron sulphate, etc., and finally dyed either by immersion or a brushing process. Paraphenylenediamine and similar compounds are among those used for the dyeing of hair.

As **antiseptics** several dyestuffs are used in medicine for this purpose. Crystal violet is used as an external application for staphylococcal infections and, internally, for the treatment of threadworm. Brilliant green, another derivative of triphenylmethane, is also used externally for its antiseptic properties. An important group is the acridine dyes which include Acriflavine and Proflavine (*q.v.*). Triple dye solution, consisting of an aqueous solution of crystal violet, brilliant green, and acriflavine, has been used for the treatment of burns and for skin sterilization. (See Antiseptics, Bacteria, and Disinfectant.)

*References:* *Dyeing with Coal-Tar Dyestuffs*, by C. M. Whittaker (Baillière, Tindall and Cox, London); *A Textbook of Dye Chemistry*, by Von Georgievics and Grandmougin (E. Benn, London); *Chemistry of Dyeing*, by J. K. Wood (Gurney and Jackson, London); *Dyeing and Cleaning*, by F. J. Farrel (C. Griffin and Co., Ltd., London); *Fundamental Processes of Dye Chemistry*, by Fierz-David and Blangey (Interscience Publishers, New York); see also Intermediates, Plant Colouring Matters, Nigrosines, Rosanilines, Safranines, and Textiles.

**DYNAMITE** — See Explosives.

**DYSPROSIUM (Dy)** — Atomic weight, 162.46. See Elements for other data. One of the members of the yttrium group of the rare earth elements. Occurs in the mineral *gadolinite*.

**DYSTECTIC MIXTURE** — The correlative of eutectic mixture, being a mixture of definite proportions of two or more substances of constant melting-point, constituting the maximum melting-point of any mixture of them. The addition of any one of the constituents lowers the melting point. Generally considered as representing in composition a chemical compound.

**EARTH** — The elements making up the chemical composition of the earth have been studied as to their abundance by F. W. Clarke as a member of the U.S. Geological Survey, and his conclusions are presented.

The elements named above are designated the petrogenic or rock-forming elements, and the remaining elements, including copper, zinc, and all elements beyond iron (except barium and strontium, which are included above, and possibly nickel and zirconium) in the periodic arrangement of the elements are designated metallogenic elements (Clarke and Washington). The petrogenic elements form mostly oxides and oxygen salts, whereas the metallogenic elements form mostly sulphides and arsenides.

Barnett (1924) has estimated that the interior of the earth, *i.e.*,

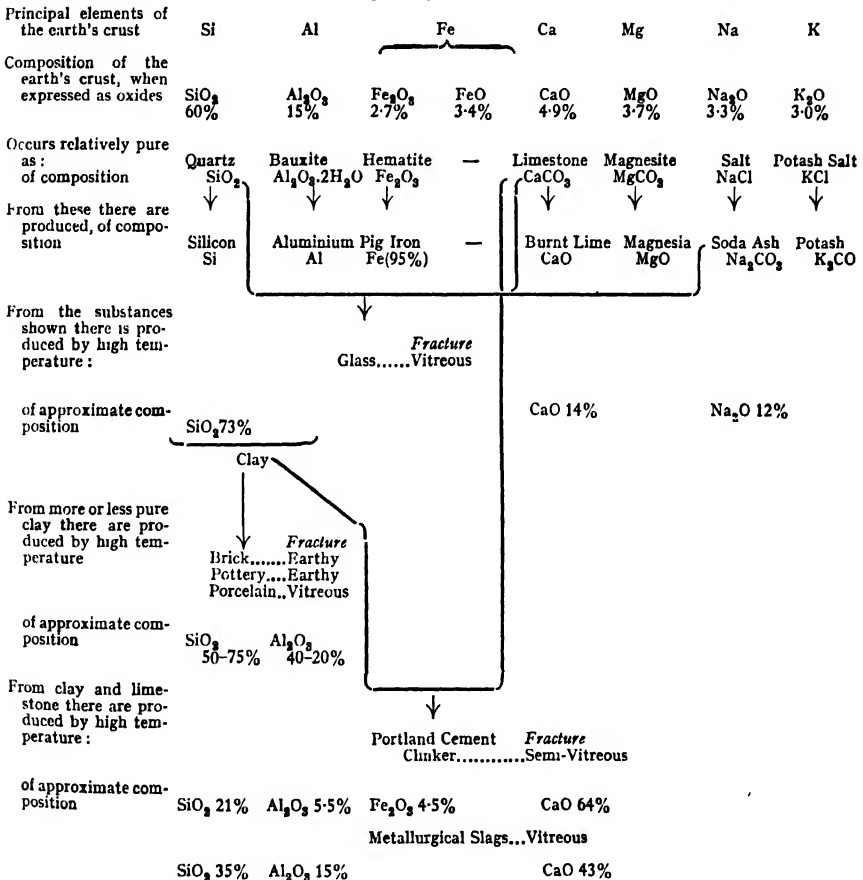
77.5 per cent. of the whole, is an irregular core of metallic substances—iron 90 per cent. and nickel *plus* cobalt *plus* copper 7 per cent.—in a fused state, probably more or less mixed with silicates, whilst an irregular sheet of silicates as slag, more or less mixed with metal, constitutes the remaining outer shell of 22.5 per cent. of the whole.

The principal elements of the earth's crust have important industrial chemical relations, which are shown, in brief, in the accompanying chart.

## PRINCIPAL ELEMENTS OF THE EARTH'S CRUST

### CHART SHOWING SOME IMPORTANT NATURAL AND MANUFACTURED PRODUCTS

Arranged by the Editor.



*References: Geochemistry: A Survey of the Chemistry of the Earth, by Kalervo Rankama and Th. G. Sahama (University of Chicago Press); The Data of Geochemistry, by F. W. Clarke (U.S. Geol. Survey, Bull., 695, Washington).*

ELEMENTS IN THE ORDER OF ABUNDANCE IN KNOWN  
TERRESTRIAL MATTER

Authority: *F. W. Clarke*

Element	Per cent.			
Oxygen .. .. .	50.02			
Silicon .. .. .	25.80			
Aluminium .. .. .	7.30			
Iron .. .. .	4.18			
Calcium .. .. .	3.22			
Sodium .. .. .	2.36			
Potassium .. .. .	2.28			
Magnesium .. .. .	2.08	97.24		
Hydrogen .. .. .	0.95			
Titanium .. .. .	0.43			
Chlorine .. .. .	0.20			
Carbon .. .. .	0.18			
Phosphorus .. .. .	0.11			
Sulphur .. .. .	0.11			
Fluorine .. .. .	0.10			
Manganese .. .. .	0.08			
Barium .. .. .	0.08			
Nitrogen .. .. .	0.03			
Strontium .. .. .	0.02	2.29	99.53	
All other elements .. .. .			0.47	
Total .. .. .			100.00	

**EARTH-NUT OIL** — See Arachis Oil, and Nut Oils.

**EARTH WAX (Cerasine)** — See Waxes.

**EARTHENWARE** — See Porcelain.

**EAST INDIA RESIN** — See Gums and Resins.

**EAU DE COLOGNE** — A popular solution of various essential oils (including neroli, bergamot, citron, lavender, lemon, orange, and rosemary, etc.) in alcohol, prepared as a perfume by many recipes; a small quantity of the oil of Malabar cardamoms is sometimes incorporated. The methods of manufacture of fine brands are closely guarded secrets.

**EAU DE JAVELLE and EAU DE LABARRAQUE** — Dilute solutions of potassium and sodium hypochlorites at one time commonly used in France for bleaching and disinfecting purposes. They can be severally prepared by treating a solution of calcium hypochlorite with one of potassium or sodium carbonate and filtering off the precipitated calcium carbonate. (See Dakin's Solution.)

**EBONITE** — See Rubber (Vulcanite).

**EBONY** — The black heart-wood of *Diospyros ebenum*, which grows in Ceylon, Madagascar, etc., is the best-known variety, of which there are a number of kinds derived from various species.

**EBULLIOSCOPE (Ebuliscope)** — An apparatus for determining the boiling-points of liquids ; also for determining the strength of solutions by means of the temperatures at which they boil.

**ECHITAMINE (DITAINE)** ( $C_{22}H_{28}O_4N_2$ ) — A crystalline alkaloid contained in the bark of *Alstonia scholaris* R. Br., and other similar species. It melts at 105° C., and is soluble in water, alcohol, and acetone. (See *The Plant Alkaloids*, by Henry (Churchill, London).)

**ECONOMIC ASPECTS** — The natural resources of the various countries of the world have been and are being studied with intense care on account of "the prospects of peace." This is in marked contrast to their study "on account of the prospects of war and its consequences to civilian populations and military undertakings" as stated in the preceding edition of this work. What those consequences proved to be is all too well known. A comparable effort towards peace by men of good will in industry and government would do much to alleviate the hardship and suffering that war produced. The part played in this situation by economics is of the greatest importance, and possibly it is decisive.

To portray the role that economics plays in chemical fields is a puzzling task. Puzzling as it is, it is not to be lightly thrust aside, and so a serious attempt is made here to supply for the reader the salient facts concerning the production (as to country and quantity) of materials related to chemistry. Food materials might well be considered first, but it was regretfully decided that this phase of the subject is much too complicated and involved to be justly and adequately dealt with here. It is different, however, in regard to fuels and fertilizers, to metallic ores and metals, and to salt, sulphur, and cement. Regarding these materials considerable pertinent and valuable information is available. World production data have been assembled and shown in their respective places for the following 43 chemical commodities, namely :

Aluminium	Magnesium
Aluminium ore (see Bauxite under Aluminium)	Manganese ore (see Manganese)
Antimony	Mercury
Arsenic trioxide (see Arsenic)	Molybdenum ore (see Molybdenum)
Asbestos	Nickel ore (see Nickel)
Barite (see Barium)	Nitrogen
Bauxite (see Aluminium)	Petroleum
Bismuth	Phosphate, rock (see Calcium Phosphate under Calcium)
Cadmium	Platinum metals (see Platinum)
Cement	Potash (see Potassium)
Chromite (see Chromium)	Pyrites (see Sulphur)
Coal	Quicksilver (see Mercury)
Cobalt ore (see Cobalt)	Salt (see Sodium Chloride under Sodium)
Copper	Sodium chloride (see Sodium)
Feldspar	

Fluorspar (see Calcium Fluoride under Calcium; also named Fluorite)	Silver
Gold	Sulphur
Graphite (see Carbon)	Tin
Gypsum (see Calcium Sulphate under Calcium)	Tin ore (see Tin)
Iron, pig	Titanium, concentrates (see Titanium)
Iron ore (see Iron)	Tungsten, concentrates (see Tungsten)
Lead	Vanadium ore (see Vanadium)
Lignite (see Coal)	Zinc

The number of countries considered as having placements of these 43 chemical commodities (see below) is 73. Two different arrangements are presented *here* of data contained in the above individual tables. The first arrangement is of selected commodities by producing country, by amount (all in metric tons), and by percentage of world production; and the second, the relative placement standing by countries under their respective continents. Practically all the data are for the annual average of the three-year period, 1937-1939, which, it is believed, gives *the most representative world picture that can be had*. Such arrangements as these will serve to display dependable information for those who wish to compare later and current statistics which are considered to be outside the scope of this monograph. The conclusion is obvious, namely, the very great *interdependence* of the various industrial and governmental parts of the world.

#### SELECTED CHEMICAL COMMODITIES BY PRODUCING COUNTRIES AND THEIR RESPECTIVE PRODUCTIONS

<b>Fuels</b>	Producing Country	Metric Tons	Per Cent. of World Pro- duction
Coal	U.S.A.	402,000,000	
	Germany	401,000,000	
	United Kingdom	233,000,000	
	U.S.S.R.	143,000,000	
	France	47,000,000	
	Japan	40,000,000	
	Poland	37,000,000	
		<hr/> 1,303,000,000	<b>84</b>
Petroleum	U.S.A.	174,100,000	
	U.S.S.R.	28,300,000	
	Venezuela	26,900,000	
	Iran and Iraq	15,300,000	
	Indonesia	8,100,000	
	Rumania	6,800,000	
	Mexico	5,900,000	
		<hr/> 265,400,000	<b>94</b>

SELECTED CHEMICAL COMMODITIES (*cont.*)

<b>Fertilizers</b>	Producing Country	Metric Tons		Per Cent. of World Pro- duction
Nitrogen	Japan	421,000		
	Germany (estimate)	400,000		
	Chile	225,000		
	U.S.A.	187,000		
	France	149,500		
	United Kingdom	131,500		
		<hr/>	1,514,000	62
Phosphate, rock	Mediterranean Africa	4,500,000		
	U.S.A.	3,900,000		
	U.S.S.R.	1,600,000		
		<hr/>	10,000,000	86
Potash (K <sub>2</sub> O content)	Germany	2,070,000		
	France	560,000		
	U.S.A.	280,000		
	U.S.S.R.	200,000		
	Poland	100,000		
		<hr/>	3,210,000	98
<b>Metals and Their Ores</b>	Producing Country	Metric Ton		Per Cent. of World Pro- duction
Aluminium ore	France	687,000		
	Hungary	556,000		
	Netherlands Guiana	424,000		
	British Guiana	391,000		
	Italy	381,000		
	U.S.A.	376,000		
	Yugoslavia	355,000		
		<hr/>	3,170,000	80
Aluminium metal	Germany-Austria	160,000		
	U.S.A.	137,000		
	Canada	61,000		
	France	43,000		
	U.S.S.R.	43,000		
		<hr/>	444,000	78
Copper ore (Cu con- tent)	U.S.A.	620,000		
	Chile	370,000		
	Canada	260,000		
	Northern Rhodesia	250,000		
		<hr/>	1,500,000	70

SELECTED CHEMICAL COMMODITIES (*cont.*)

<b>Metals and Their Ores</b>	Producing Country	Metric Tons		Per cent. of World Pro- duction
Copper metal	U.S.A.	700,000		
	Chile	350,000		
	Canada	220,000		
	Northern Rhodesia	210,000		
	Belgian Congo	130,000		
	U.S.S.R.	100,000		
	Japan	100,000		
		<hr/>	1,810,000	83
Iron ore	U.S.A.	51,700,000		
	France	35,000,000		
	U.S.S.R.	26,000,000		
	Sweden	14,200,000		
	United Kingdom	13,700,000		
	Germany-Austria	13,300,000		
		<hr/>	153,900,000	80
Iron, pig	U.S.A.	29,800,000		
	Germany-Austria	18,400,000		
	U.S.S.R.	15,000,000		
	United Kingdom	7,900,000		
	France	7,300,000		
	Belgium-Luxem- burg	5,000,000		
	Japan	2,900,000		
		<hr/>	86,300,000	90
Lead metal	U.S.A.	386,000		
	Australia	243,000		
	Mexico	236,000		
	Germany-Austria	178,000		
	Canada	145,000		
	Belgium	95,000		
		<hr/>	1,283,000	76
Manganese ore	U.S.S.R.	2,500,000		
	India and Pakistan	970,000		
	Union of S. Africa	534,000		
	Gold Coast	444,000		
	Brazil	223,000		
	Egypt	153,000		
		<hr/>	4,824,000	88
Nickel ore	Canada	100,000		
	New Caledonia	11,000		
	U.S.S.R.	2,000		
		<hr/>	113,000	96

SELECTED CHEMICAL COMMODITIES (*cont.*)

<b>Metals and Their Ores</b>	Producing Country	Metric Tons		Per Cent. of World Pro- duction.
Tin ore (Sn content)	Malaya	58,000		
	Indonesia	31,000		
	Bolivia	26,000		
	Thailand	16,000		
	China	12,000		
	Nigeria	10,000		
		<hr/>	153,000	85
Tin metal	Malaya	80,000		
	United Kingdom	32,000		
	Netherlands	23,000		
	Indonesia	12,000		
	China	11,000		
		<hr/>	158,000	89
Zinc metal	U.S.A.	443,000		
	Belgium	207,000		
	Germany	190,000		
	Canada	153,000		
	Poland	111,000		
	U.S.S.R.	77,000		
	Australia	71,000		
		<hr/>	1,252,000	78
<b>Salt, Sulphur, and Cement</b>	Producing Country	Metric Tons		Per cent. of World Pro- duction
Salt	U.S.A.	8,000,000		
	U.S.S.R.	4,500,000		
	Germany	3,500,000		
	United Kingdom	3,000,000		
	China	3,000,000		
	France	2,200,000		
	India and Pakistan	1,600,000		
	Italy	1,500,000		
		<hr/>	27,300,000	80
Sulphur	U.S.A.	2,700,000		
	Italy	340,000		
	Japan	200,000		
		<hr/>	3,240,000	99
Cement	U.S.A.	19,900,000		
	Germany-Austria	14,700,000		
	United Kingdom	7,600,000		
	Japan	6,000,000		
	U.S.S.R.	5,600,000		
	Italy	4,600,000		
	France	4,300,000		
		<hr/>	62,700,000	71

RELATIVE PLACEMENT STANDING FOR 43 CHEMICAL COMMODITIES  
BY COUNTRIES

*Note* : Countries are arranged alphabetically under their respective continents.

### EUROPE

*Belgium-Luxemburg* : Arsenic trioxide 5th, cadmium 5th, cement 8th, coal 8th, copper 7th, iron 6th, iron ore 7th, lead 6th, tin 6th, zinc 2nd.

*Czechoslovakia* : Antimony 5th, cement 11th, coal 10th, feldspar 3rd, graphite 7th, iron 9th, iron ore 16th, mercury 6th, salt 18th, silver 20th.

*Denmark* : Cement 19th.

*Finland* : Asbestos 7th, cement 23rd, copper 12th, feldspar 8th.

*France* : Aluminium 4th, aluminium ore 1st, arsenic trioxide 3rd, cadmium 12th, cement 7th, coal 5th, fluorspar 4th, gypsum 2nd, iron 5th, iron ore 2nd, lead 9th, magnesium 4th, nitrogen 5th, potash 2nd, salt 6th, zinc 8th.

*Germany-Austria* : Aluminium 1st, arsenic trioxide 8th, barite 1st, cadmium 3rd, cement 2nd, coal 2nd, copper 8th, copper ore 11th, feldspar 7th, fluorspar 1st, graphite 2nd, gypsum 5th, iron 2nd, iron ore 6th, lead 4th, magnesium 1st, nitrogen 2nd, potash 1st, pyrites 6th, salt 3rd, silver 9th, tin 7th, zinc 3rd.

*Greece* : Aluminium ore 10th, barite 5th, chromite 9th, nickel ore 4th, pyrites 9th.

*Hungary* : Aluminium ore 2nd, iron 15th, manganese ore 13th.

*Italy* : Aluminium 8th, aluminium ore 5th, antimony 7th, asbestos 6th, barite 4th, cadmium 10th, cement 6th, feldspar 6th, fluorspar 7th, graphite 6th, gypsum 6th, iron 10th, lead 9th, magnesium 8th, manganese ore 9th, mercury 1st, pyrites 3rd, salt 8th, silver 22nd, sulphur 2nd, zinc 13th.

*Latvia* : Gypsum 7th.

*Netherlands* : Cement 23rd, coal 12th, iron 17th, tin 3rd, zinc 14th.

*Norway* : Aluminium 6th, cadmium 7th, copper 12th, feldspar 4th, fluorspar 11th, graphite 9th, iron 18th, molybdenum ore 3rd, nickel ore 4th, pyrites 3rd, titanium ore 4th, zinc 11th.

*Poland* : Cadmium 9th, cement 9th, coal 7th, iron 10th, potash 5th, salt 11th, zinc 5th.

*Portugal* : Pyrites 5th, tin 10th, tungsten ore 4th.

*Rumania* : Cement 23rd, feldspar 10th, gypsum 10th, iron 20th, manganese ore 8th, petroleum 6th, salt 14th, silver 22nd.

*Spain* : Barite 9th, cement 17th, copper 12th, copper ore 11th, fluorspar 9th, iron 15th, iron ore 11th, lead 11th, mercury 2nd, potash 6th, pyrites 1st, salt 12th.

*Sweden* : Arsenic trioxide 3rd, cement 11th, copper 12th, feldspar 2nd, iron 13th, iron ore 4th, pyrites 9th, silver 20th, tungsten ore 11th.

*Switzerland* : Aluminium 7th, cement 21st, magnesium 7th.

*United Kingdom* : Aluminium 9th, barite 3rd, cadmium 11th, cement 3rd, coal 3rd, copper 12th, fluorspar 5th, gypsum 3rd, iron 4th, iron ore 5th, magnesium 2nd, nitrogen 6th, salt 4th, tin 2nd, tin ore 10th, tungsten ore 11th, zinc 9th.

*Yugoslavia* : Aluminium ore 7th, antimony 4th, cement 19th, chromite 7th, copper 9th, copper ore 8th, silver 15th.

### U.S.S.R.

Aluminium 4th, aluminium ore 8th, asbestos 2nd, cement 5th, chromite 1st, coal 4th, copper 6th, copper ore 6th, fluorspar 3rd, gold 2nd, iron 3rd, iron ore 3rd, lead 8th, magnesium 6th, manganese ore 1st, mercury 4th, nickel ore 3rd, petroleum 2nd, phosphate rock 3rd, platinum 2nd, potash 4th, pyrites 2nd, salt 2nd, silver 8th, zinc 6th.

### NORTH AMERICA

*Canada* : Aluminium 3rd, asbestos 1st, bismuth 4th, cadmium 4th, cement 14th, cobalt ore 4th, copper 3rd, copper ore 3rd, feldspar 5th, gold 3rd, graphite 10th, gypsum 3rd, iron 10th, lead 5th, nickel ore 1st, platinum 1st, pyrites 11th, salt 13th, silver 3rd, titanium ore 3rd, zinc 4th.

*Cuba* : Barite 8th, chromite 6th.

*Honduras* : Silver 11th.

*Mexico* : Antimony 3rd, arsenic trioxide 2nd, bismuth 3rd, cadmium 2nd, copper 9th, copper ore 8th, gold 7th, graphite 5th, iron 20th, lead 3rd, mercury 5th, molybdenum ore 2nd, petroleum 7th, silver 1st, tungsten ore 14th, vanadium ore 5th, zinc 12th

*Newfoundland* : Fluorspar 8th, iron ore 13th, silver 16th.

*Trinidad* : Petroleum 10th.

*U.S.A.* : Aluminium 2nd, aluminium ore 6th, antimony 7th, arsenic trioxide 1st, asbestos 4th, barite 2nd, bismuth 1st, cadmium 1st, cement 1st, coal 1st, copper 1st, copper ore 1st, feldspar 1st, fluorspar 2nd, gold 4th, graphite 8th, gypsum 1st, iron 1st, iron ore 1st, lead 1st, magnesium 3rd, manganese ore 10th, mercury 3rd, molybdenum ore 1st, nitrogen 4th, petroleum 1st, phosphate rock 1st, platinum 4th, potash 3rd, pyrites 6th, salt 1st, silver 2nd, sulphur 1st, titanium ore 2nd, tungsten ore 3rd, vanadium ore 2nd, zinc 1st.

### SOUTH AMERICA

*Argentina* : Cement 10th, petroleum 11th, salt 14th, silver 12th, tin ore 10th, tungsten ore 6th.

*Bolivia* : Antimony 2nd, silver 7th, tin ore 3rd.

*Brazil* : Cement 21st, manganese ore 5th, salt 9th, titanium ore 6th.

*British Guiana* : Aluminium ore 4th.

*Chile* : Copper 2nd, copper ore 2nd, iron ore 14th, manganese ore 14th, nitrogen 3rd, silver 16th, sulphur 4th.

*Colombia* : Gold 12th, petroleum 9th, platinum 5th.

*Netherlands Guiana* : Aluminium ore 3rd.

*Peru* : Antimony 6th, bismuth 2nd, copper 9th, copper ore 8th, lead 12th, petroleum 12th, silver 4th, tungsten ore 14th, vanadium ore 1st.

*Venezuela* : Petroleum 3rd.

## ASIA

*Aden* : Salt 14th.

*Burma* : Cobalt ore 4th, lead 7th, nickel ore 4th, silver 10th, tin ore 8th, tungsten ore 2nd.

*Ceylon* : Graphite 3rd.

*China* : Antimony 1st, salt 4th, tin 5th, tin ore 5th, tungsten ore 1st.

*Cyprus* : Asbestos 5th, copper ore 11th, pyrites 6th.

*India and Pakistan* : Barite 6th, cement 11th, chromite 8th, coal 9th, graphite 11th, gypsum 10th, iron 8th, iron ore 8th, manganese ore 2nd, salt 7th, titanium ore 1st.

*Indochina* : Salt 18th, tungsten ore 9th.

*Indonesia* : Aluminium ore 9th, manganese ore 15th, petroleum 5th, sulphur 4th, tin 4th, tin ore 2nd.

*Iran (Persia)* : Petroleum 4th.

*Iraq* : Petroleum 8th

*Japan* : Aluminium 10th, arsenic trioxide 5th, cement 4th, coal 6th, copper 6th, copper ore 6th, gold 10th, gypsum 10th, iron 7th, magnesium 5th, nitrogen 1st, salt 9th, silver 6th, sulphur 3rd, tin ore 10th, zinc 10th.

*Korea (Chosen)* : Barite 7th, cement 14th, fluorspar 6th, gold 7th, graphite 1st, iron 18th, salt 18th, silver 14th, tungsten ore 5th.

*Malaya* : Iron ore 12th, manganese ore 10th, tin 1st, tin ore 1st, titanium ore 8th, tungsten ore 6th.

*Manchuria* : Cement 17th, iron 13th.

*Palestine* : Potash 6th.

*Philippines* : Chromite 5th, gold 6th, manganese ore 12th, silver 18th.

*Thailand (Siam)* : Tin ore 4th, tungsten ore 11th.

*Turkey* : Antimony 10th, chromite 2nd, salt 18th.

## AFRICA

*Algeria* : Antimony 7th, barite 11th, iron ore 9th, phosphate rock 6th.

*Belgian Congo* : Cobalt ore 2nd, copper 5th, copper ore 5th, gold 12th, silver 13th, tin 9th, tin ore 7th.

*Egypt* : Gypsum 7th, manganese ore 6th, phosphate rock 7th, salt 14th.

*French Cameroon* : Titanium ore 7th.

*French Morocco* : Cobalt ore 3rd, graphite 12th, manganese ore 7th, phosphate rock 3rd.

*Gold Coast* : Gold 10th, manganese ore 4th.

*Madagascar* : Graphite 4th.

*Nigeria* : Tin ore 6th.

*Northern Rhodesia* : Cobalt ore 1st, copper 4th, copper ore 4th, vanadium ore 4th, zinc 15th.

*Senegal* : Titanium ore 9th.

*Southern Rhodesia* : Asbestos 3rd, chromite 2nd, gold 7th, tungsten ore 10th.

*South-West Africa* : Cadmium 7th, vanadium ore 3rd.

*Spanish Morocco* : Iron ore 16th.

*Tunisia* : Fluorspar 11th, lead 12th, phosphate rock 2nd.

*Union of South Africa* : Asbestos 3rd, cement 14th, chromite 4th, coal 10th, copper 12th, fluorspar 10th, gold 1st, manganese ore 3rd, platinum 3rd, silver 18th, tungsten ore 14th.

## OCEANIA

*Australia* : Antimony 10th, arsenic trioxide 7th, barite 10th, cadmium 6th, cement 17th, feldspar 9th, gold 5th, gypsum 7th, iron 10th, iron ore 10th, lead 2nd, silver 5th, tin 8th, tin ore 9th, titanium ore 5th, tungsten ore 6th, zinc 7th.

*Nauru and Ocean Islands* : Phosphate rock 5th.

*New Caledonia* : Chromite 9th, nickel ore 2nd.

## SUMMARY :

Continent	Number of Countries considered as having Placements of 43 Chemical Com-modities	Number of Placements by Countries of the 43 Com-modities	Total Number of Commodity Placements by Countries
Europe, exclusive of U.S.S.R. . . . .	20	37*	177
U.S.S.R. . . . .	1	25	25
North America . . . . .	7	41†	82
South America . . . . .	9	24	35
Asia, exclusive of U.S.S.R. . . . .	18	36‡	80
Africa . . . . .	15	27	51
Oceania . . . . .	3	19	20
	73		470

\* Only bismuth, cobalt ore, gold, phosphate rock, platinum, vanadium not placing.

† Only tin, tin ore not placing.

‡ Only bismuth, cadmium, mercury, molybdenum ore, phosphate rock, platinum, vanadium ore not placing.

Note : A few minor placements shown in the commodity tables were purposely not considered in the above tabulation, for example, those countries producing less than 0.5 million metric tons of cement as their annual average.

References : *World Atlas of Commercial Geology* (U.S. Geological Survey); *Mineral Raw Materials* (McGraw-Hill Book Co., New York), for the sources of 32 metals and their commerce in the twelve leading industrial countries; *Commodities of Commerce, Vegetable, Animal, Mineral, and Synthetic*, by J. H. Vanstone (1934); *World Minerals and World Politics*, by C. K. Leith (McGraw-Hill Book Co., New York, 1931); *World Minerals and World Peace*, by C. K. Leith et al., 1943 (Brookings Institution, Washington, D.C.); *Minerals Yearbook*, U.S. Bureau of Mines (Superintendent of Documents, Washington, D.C.); *Commodities in Industry* (Commodity Research Bureau, New York); *Chemical Facts and Figures*, 1946 (Manufacturing Chemists' Association of the United States, Washington, D.C.); *Synthetic Organic Chemicals* (annual), U.S. Tariff Commission (Superintendent of Documents, Washington, D.C.); *U.S. Census of Manufactures* (Superintendent of Documents, Washington, D.C.); *The Mineral Industry of the British Empire and Foreign Countries*, Imperial Institute (H.M. Stationery Office, London); *Strategic Minerals*, by J. B. De Mille (McGraw-Hill Book Co., New York) for uses, world output, stockpiles, and procurement; *Strategic Mineral Supplies*, by G. A. Roush (McGraw-Hill Book Co., New York); *Forest Resources of the World*, by R. Zon and W. N. Sparhawk (McGraw-Hill Book Co., New York).

**EDUCT** — A body or cleavage product, separated or brought to light by the splitting up, as by hydrolysis, of a more complex substance in which it previously existed in chemical association, and not otherwise originated by the decomposition.

**EFFERVESCENCE** — Escape of gas from a liquid or mixture—as, for example, when hydrochloric acid is poured on marble, carbon dioxide gas is evolved ; or as, again, when soda-water (which is water charged under pressure with the same gas) is allowed to escape from a siphon.

**EFFLORESCENCE** — Salts which lose a part of their water of crystallization on exposure to the air, and thereby become coated with a pulverulent deposit due to this change, are described as efflorescent. Common washing soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), for example, by efflorescence loses 9 out of its 10 molecules of water and becomes reduced to the carbonate of sodium (or different crystalline form) represented by the formula  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . That is because its vapour pressure is greater than that of the atmospheric aqueous vapour ; on the other hand, some crystalline salts, such as nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), absorb moisture from the air. (See Crystals, Deliquescence, and Drying.)

**EGGS** are nutritious articles of food. Eggs for storage should not be more than a week old, and the temperature should be between  $0^\circ$  and  $0.6^\circ \text{C}$ ., the air being kept humid, with free circulation ; evaporation of the egg moisture can be checked by use of various coating solutions, aluminium soap in pentane being one mixture recommended (T. Moran and R. Piqué, H.M. Stationery Office, 1926). Dried egg contains from 38 to 40 per cent. oil and phosphatides, about 44 to 44½ per cent. albuminoids, and 4 to 5 per cent. carbohydrates.

The shell of birds' eggs consists for the most part of calcium carbonate (about 90 per cent.), calcium and magnesium phosphates (about 6 per cent.), and animal matter and sulphur (about 4 to 5 per cent.).

The white of egg is albumin, whilst the yolk is of complicated composition, containing fatty matters, lecithin (a phosphatide present in brain matter), cholesterol (about 1.36 per cent.), etc.

The eggs and roes of fishes are, to some extent, of somewhat similar composition, and equally valuable as foods.

Both the albumin and the yolks of eggs are used in many industries. The yolks of eggs can be preserved without change in the nature of their coagulation if the temperature be not allowed to fall below  $-6^\circ \text{C}$ . ; they can be used in soap-making, as, apart from the olein contained in them, the constituent lecithin is decomposed by hydrolysis to yield stearic acid, oleic acid, phosphoric acid, glycerol, and choline, and the first two named acids become converted into soap.

A protein substance named "livetin" is stated to be present in egg yolk, in addition to lecithin-vitellin, and that it has the properties of a pseudo-globulin.

The composition of eggs is given by J. Grosfeld in *B.C.A.*, B, 1933, 476 ; and by L. G. Mitchell *et al.* in *Analyst*, 58, 480 (1933).

**EGO OIL** — From seeds of "Egonoki" (*Styrax japonica*), indigenous in Japan.

**EINSTEIN EQUATION** — See Energy, and Nuclear Chemistry.

**EICOSANOIC ACID** ( $C_{19}H_{39}.COOH$ ) — A constituent of Rambutan tallow, the fatty constituent of the seeds of *Nephelium lappaceum*; it can also be prepared from erucic acid.

**EKA** — Prefix being the Sanskrit numeral one. Gallium is the element which Mendelejeff predicted by name "eka-aluminium."

**"EKASALT"** — Sodium malate, which tastes much like sodium chloride, and is partially substituted for the latter as a condiment when the chloride produces undesirable effects.

**ELÆOPTENES** — See Stearoptenes.

**ELÆOSTEARIC ACIDS** ( $\alpha$  and  $\beta$ ) are stated to be stereo-isomeric linolenic acids. The constitution of the  $\alpha$  variety is alleged to have been proved as  $CH_3.(CH_2)_8.(CH:CH)_3.(CH_2)_7.CO_2H$ . (See Tung Oil.)

**ELAÏDIC ACID** — See Oleic Acid.

**ELASTICITY** — Capability of being stretched and resumption of original shape and dimension upon cessation of the force used to alter the original form. (See Rubber).

**ELASTOMERS** — Materials that can be stretched repeatedly to 150 per cent. or more of their initial length and thereafter will return rapidly and with force to the approximate original length. Synthetic elastomers include synthetic rubbers (see same).

*Reference: Elastomers and Plastomers: Their Chemistry and Technology*, by R. Houwink, editor (Elsevier Publishing Co., New York and London.)

**ELECTRIC BATTERIES** — See Electricity.

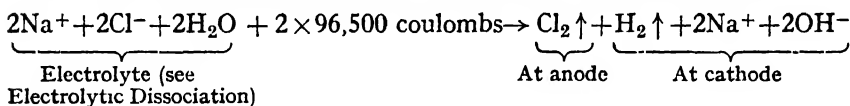
**ELECTRICAL CONDUCTIVITY** (See Elements for data for individual elements).—The equivalent conductance at infinite dilution of individual ions at 25° C. is as follows:

H <sup>+</sup>	..	..	350	$\frac{1}{2}Mg^{++}$	..	53	Br <sup>-</sup>	..	..	78
K <sup>+</sup>	..	..	74	Na <sup>+</sup>	..	50	I <sup>-</sup>	..	..	77
NH <sub>4</sub> <sup>+</sup>	..	..	73	Li <sup>+</sup>	..	39	Cl <sup>-</sup>	..	..	76
$\frac{1}{2}Ba^{++}$	..	..	64	OH <sup>-</sup>	..	198	NO <sub>3</sub> <sup>-</sup>	..	..	71
Ag <sup>+</sup>	..	..	62	$\frac{1}{2}SO_4^{-}$	..	80	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	..	..	41
$\frac{1}{2}Ca^{++}$	..	..	60							

**ELECTRICAL PRECIPITATION OF GASES** — See Cottrell Precipitating Plant.

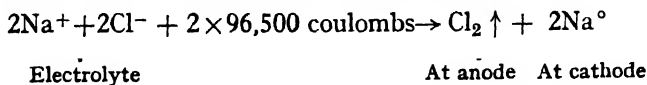
**ELECTRICITY (Electrochemical Aspects)** — The application of electricity to chemical reactions involves the use of both direct and alternating currents, the former being demanded for (1) directly produced reactions in electrolytes (that is, water solutions of salts, acids, and bases, or fused salts); and the converse phenomenon encountered when (2) in batteries a chemical reaction generates electricity. Electric current is also desirable (3) for the production of very high temperatures, such as are requisite for converting calcium oxide plus carbon into calcium carbide.

The principles concerned with (1) and (2) are related (A) to the *amount* of current involved, and (B) to the *intensity* of the current. Consider the case of sodium chloride-water solution as the electrolyte. When this is subjected to direct current there must be provided adequate means for supplying the electrolyte and the current. Therefore, for the latter there must be an "in" electrode (positive anode, say, of graphite, chosen because it resists chemical attack well and is electrically conducting), and an "out" electrode (negative cathode, say, of iron or steel). If the anode and cathode compartments are not separated and the electrolyte is well mixed, the product is sodium hypochlorite (NaOCl). If, on the other hand, the anode and cathode compartments are separated mechanically (but not electrically) by means of a porous diaphragm, usually of asbestos paper, the products are chlorine gas ( $\text{Cl}_2$ ) at the anode and hydrogen gas ( $\text{H}_2$ ) plus sodium hydroxide (NaOH) at the cathode, all simultaneously formed by the action of the current. For each one equivalent of chemical change there is consumed 96,500 coulombs (96,500 amperes  $\times$  seconds, or 26.7 amperes  $\times$  hours, or 1.00000 faraday) of electricity, in accordance with the well-known Faraday's law; and there must be applied an electromotive force above the critical value, which value in this particular example is 2.2 volts. In the form of an electrochemical equation, where two equivalents are shown, this may be represented thus:



which says that the yield from  $2 \times 58.5$  grams of sodium chloride plus  $2 \times 18$  grams of water reacting is 71 grams of chlorine gas plus 2 grams of hydrogen gas plus  $2 \times 40$  grams of sodium hydroxide in solution, by the consumption of  $2 \times 96,500$  coulombs or  $2 \times 96,500$  ampere  $\times$  seconds of direct current (applied at a voltage above the critical value of 2.2 volts, which is understood but not expressed in the equation). Only part of the sodium chloride is commonly converted to sodium hydroxide (see Hittorf, below), and the recovery of this product is accomplished by evaporating until the residual sodium chloride crystallizes out (sodium chloride is only slightly soluble in concentrated sodium hydroxide solution) and is filtered off, whereupon the resulting solution of sodium hydroxide is either used as such or evaporated to dryness for the solid. The residual sodium chloride is used again.

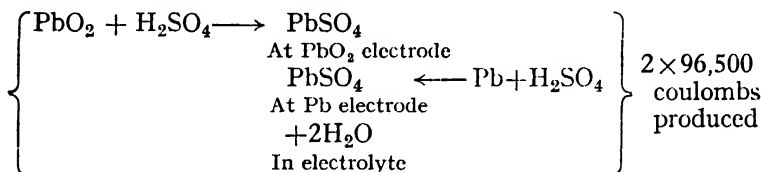
The *coulomb* or ampere (so-called current or quantity) *factor* applies to all electrochemical reactions, as stated previously, so that each gram equivalent (unit change of valence) of chemical change consumes 96,500 coulombs. If fused or molten sodium chloride (m.p.  $800^\circ \text{C}.$ ) is the electrolyte the electrochemical equation is:



which says that the yield from  $2 \times 58.5$  grams of sodium chloride is 71 grams of chlorine gas plus  $2 \times 23$  grams of sodium metal by the consumption of  $2 \times 96,500$  coulombs or  $2 \times 96,500$  amperes  $\times$  seconds of direct current (applied at a voltage above the critical value).

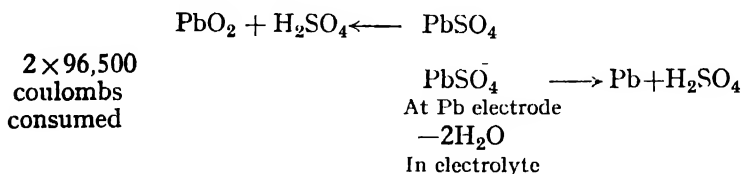
The *voltage* (so-called electromotive force or intensity) *factor* is usually of the order of only a few volts, but is characteristic of each reaction. Since current is valued on an ampere  $\times$  volt  $\times$  time basis the lowest voltage required to operate is desired. In practice, the ampere efficiency frequently runs to 95 per cent., but the voltage efficiency is considerably lower, often 60 per cent. for the sodium chloride-water electrolyte. In this case the energy efficiency would be  $95 \times 0.60 = 57$  per cent.

In **batteries** the converse type of reaction takes place, namely, the generation of electricity from a chemical reaction at two electrodes that are (1) separated in space; (2) electrolytically connected in and by means of an electrolyte; and (3) electrically connected exterior to the electrolyte by means of a metallic conductor. When the circuit is closed a reaction takes place at the anode and another of opposite type at the cathode. To illustrate, take the case of the familiar "lead storage" battery. The lead dioxide changes to lead sulphate in the one electrode and at the same time the spongy lead changes to lead sulphate in the other electrode, the electrolyte being sulphuric acid-water solution. The electrochemical equation may be shown thus:



The two reactions occur simultaneously with accompanying dilution (decrease in concentration) of  $\text{H}_2\text{SO}_4$  (a) by removal of  $2\text{SO}_4^{--}$  and (b) by the formation of  $2\text{H}_2\text{O}$ . The factor 2 appears in the coulomb entry because  $\text{Pb}^{+4}$  of  $\text{PbO}_2$  changes to  $\text{Pb}^{+2}$  of  $\text{PbSO}_4$  and  $\text{Pb}^0$  of spongy lead changes to  $\text{Pb}^{+2}$  of  $\text{PbSO}_4$ , a net valence change of 2.

Upon charging this battery, the reverse chemical change takes place, and this can be shown thus:



The two reactions occur simultaneously with accompanying increase in concentration of  $\text{H}_2\text{SO}_4$  (a) by liberation of  $2\text{SO}_4^{--}$  and (b) by the removal of  $2\text{H}_2\text{O}$ . The coulomb factor 2 is demanded by the net valence change (which is in the opposite direction on charging to what

it is on discharging, but the same in amount). The critical voltage, which does not appear in the equation but is determined experimentally, is 2.1 volts.

Other reactions of the type where electricity produces a desired chemical reaction are numerous. *Aluminium* is produced thus: graphite or carbon anode—fused cryolite (sodium aluminium fluoride,  $\text{Na}_3\text{AlF}_6$ ) at  $1,000^\circ\text{C}$ . dissolving pure aluminium oxide ( $\text{Al}_2\text{O}_3$ ) electrolyte—iron cathode at which aluminium metal ( $\text{Al}$ , m.p.  $660^\circ\text{C}$ .) collects and is periodically drawn off underneath the electrolyte; *magnesium* thus: graphite or carbon anode—fused anhydrous magnesium chloride ( $\text{MgCl}_2$ , m.p.  $710^\circ\text{C}$ .) electrolyte—iron cathode at which magnesium metal ( $\text{Mg}$ , m.p.  $650^\circ\text{C}$ .) collects and is periodically drawn off. The energy consumption in these cases is per pound of aluminium 10–12 kilowatt  $\times$  hours, and per pound of magnesium 8–13 kilowatt  $\times$  hours; and *oxygen* and *hydrogen* by electrolysis of water and potassium hydroxide.

Electrolytic processes of winning, refining, and plating of certain metals are largely used. *Copper* is refined thus: impure copper anode—copper sulphate plus sulphuric acid plus water electrolyte—pure copper cathode, which increases in weight as the electrolysis progresses and is the desired product. The voltage required is low, 0.2–0.4 volt, principally to overcome the resistance of the electrolyte as compensating chemical reactions occur at anode ( $\text{Cu}^\circ \rightarrow \text{Cu}^{++}$ ) and at cathode ( $\text{Cu}^{++} \rightarrow \text{Cu}^\circ$ ); *lead* is refined thus: impure lead anode—lead fluosilicate plus hydrofluosilicic acid plus water electrolyte—pure lead cathode (voltage required, 0.4–0.6).

Nickel, chromium, tin, zinc, cadmium, silver, and gold are plated from various electrolytes, the composition of which is chosen for the specific task concerned; and electrotyping of printers' forms and gramophone records uses copper sulphate plus sulphuric acid plus water electrolyte to deposit metallic copper on the face of the matrix which is made electrically conducting by covering with a thin layer of graphite. The copper layer is then stripped from the matrix and backed with a low-melting-point alloy to give strength to the form. In the electrolytic deposition of rubber from its dispersion in water in the colloidal state the dispersed particles, being negatively charged, migrate toward the anode and are there deposited as a solid uniform layer. Since sulphur, pigments, and accelerators can be incorporated (Sheppard process), the layer upon drying can be vulcanized *in situ*. (See "Anode Process for Rubber Articles and Coatings" in *Ind. Eng. Chem.*, **25**, 609 (1933).)

*References*: *The Principles of Applied Electrochemistry*, by A. J. Allmand (Longmans, Green and Co., London); *Applied Electrochemistry*, by M. de K. Thompson (Macmillan Co., New York); *Industrial Electrometallurgy*, by E. K. Rideal (Baillière, Tindall and Cox, London); *Industrial Electrochemistry*, by C. L. Mantell (McGraw-Hill Book Co., New York); *Principles and Applications of Electrochemistry*, by H. J. Creighton and W. A. Koehler, 2 vol. (John Wiley and Sons, New York); *Electrochemistry, Principles and Practice*, by C. J. Brockman (D. Van Nostrand Co., New York); *The Electrochemistry*

of *Solutions*, by S. Glasstone (D. Van Nostrand Co., New York); *Electroplating*, by J. W. Urquhart (D. Van Nostrand Co., New York); *Ions, Electrons, and Ionizing Radiations*, by J. A. Crowther (Longmans, Green and Co., London and New York); *The Principles of Electrochemistry*, by D. A. MacInnes (Reinhold Publishing Corp., New York).

For the production of very high temperatures to facilitate chemical change the use of electricity is a favourite method. The production of *calcium carbide* ( $\text{CaC}_2$ ) from calcium oxide ( $\text{CaO}$ ) and carbon (C) or coke is an outstanding example in this field of chemistry; *silicon carbide* ( $\text{SiC}$ ) abrasive from silicon oxide ( $\text{SiO}_2$ ) and carbon (C) or coke is another; others are *phosphorus* from calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) plus silicon oxide ( $\text{SiO}_2$ ) plus carbon (C) or coke; and *carbon disulphide* ( $\text{CS}_2$ ) from sulphur (S) plus carbon (C) or coke. In all these examples coke is the conductor and can function as such either alone (as in  $\text{SiC}$  production) or in conjunction with an electric arc (as in the other examples). Fused aluminium oxide ( $\text{Al}_2\text{O}_3$ , m.p.  $2,050^\circ\text{C}$ .) is prepared from bauxite mineral in an electric furnace, and the product on cooling is an important abrasive (Mohs' hardness 9), (See A. G. Lobley on "Electric Furnaces for Heat Treatment" (*Chem. and Ind.*, **49**, 141 (1930); A. Stansfield, *The Electric Furnace* (McGraw-Hill Book Co., New York).

**Electrical precipitation** processes are dealt with elsewhere. (See Cottrell Precipitating Plant.)

Quantity of electricity is measured by "ampères" and pressure by "volts," and the product of the two gives the power in "watts." A thousand watts flowing a period of one hour is equal to one Board of Trade unit, and this is the accepted measure by which electricity is bought and sold. In generating stations, one kilowatt-hour of electricity can be generated by the combustion of about 1.3 pounds of coal (data for 1941). In 1919 the corresponding figure was 3.2, and in 1929 1.7.

**Ammeter** — An instrument for determining the strength of electrical currents in terms of ampères.

**Ampère (Volt  $\div$  Ohm)** — The unit of direct electric current which, when passed through a solution of silver nitrate in water, causes the deposition of silver at the rate of 0.001118 gram per second.

**Coulomb** — The unit quantity of electricity. It is the quantity that deposits 0.0011180 gram of silver from a silver salt solution. The calculation is based on 96,500 coulombs (ampere  $\times$  seconds) depositing 1 gram-atom (107.880 grams) of silver. 96,500 coulombs = 1 faraday.

**Coulombmeter** — An instrument for measuring the amount of direct electric current, by weighing the electrode before and after passage of the current, say, in a silver or copper coulombmeter, or by measuring the volume of gas, say hydrogen or oxygen, or collecting both of these gases together.

**Electromotive Force (E.M.F.) (Pressure Potential)** — Difference of potential or intensity of electric current against resistance, which can be calculated when the strength of the current ( $I$ ) in terms of ampères and the resistance ( $R$ ) in terms of ohms are known by the formula  $E \text{ (volts)} = IR$ . The unit in which electromotive force is measured is

termed the volt. Every electrolyte requires a particular minimum E.M.F. to produce continuous electrolysis. (See Electromotive Series of the Elements (Table).)

## ELECTROMOTIVE SERIES OF THE ELEMENTS

Single Potential Relative to Normal Hydrogen Electrode in Volts	Element and Accompanying Ion One-Normal Con- centration of Ion	Reaction of Metal with Acids	Reaction of Oxide Heated
—	K, Na	Displaces hydrogen	With hydrogen metal not formed
—	Ba, Ca		
-2.3	Mg/Mg <sup>++</sup>		
-1.7	Al/Al <sup>+++</sup>		
-1.05	Mn/Mn <sup>++</sup>		With hydrogen metal formed
-0.76	Zn/Zn <sup>++</sup>		
-0.44	Fe/Fe <sup>++</sup>		
-0.25	Ni/Ni <sup>++</sup>		
-0.14	Sn/Sn <sup>++</sup>	Does not dis- place hydro- gen	Metal formed
-0.13	Pb/Pb <sup>++</sup>		
0.00	H <sub>2</sub> /H <sup>+</sup>		
+0.1	Sb/Sb <sup>+++</sup>		
+0.2	Bi/Bi <sup>+++</sup>		
+0.34	Cu/Cu <sup>++</sup>		
+0.80	Ag/Ag <sup>+</sup>		
+0.85	Hg/Hg <sup>++</sup>		
+1.4	Cl <sup>-</sup> /Cl <sub>2</sub>		
+0.5	I <sup>-</sup> /I <sub>2</sub>		
+0.4	OH <sup>-</sup> /O <sub>2</sub>		
+1.2	H <sup>+</sup> /O <sub>2</sub>		

**Faraday (96,500 Coulombs)** — That quantity of electricity capable of depositing one electrochemical equivalent in grams in electrolysis. That of hydrogen is 0.00001036 gram, and the equivalents of other chemical elements are represented by the figures obtained by multiplying that of hydrogen by their gram equivalents. The gram equivalents of elements are the atomic weights divided by the valencies, except in the cases of elements that exhibit varying equivalents according to the respective valencies.

**Hittorf** — Measurement of the rate of migration of ions in solution is due to Hittorf's work (1853). H<sup>+</sup> is the swiftest, OH<sup>-</sup> next (see Electrical Conductivity). This accounts for the practice of only partially electrolysing NaCl-water electrolyte. One might say that OH<sup>-</sup> ions carry more than their share of the current and thus Cl<sup>-</sup> ions are deprived of current to produce Cl<sub>2</sub> gas—the discharge of OH<sup>-</sup> ions at the anode would produce H<sub>2</sub>O and O<sub>2</sub> gas.

**Joule's Law** — The amount of heat (*H*) developed in a conductor is proportional to the square of the current (*I*) and the resistance (*R*) of

the conductor. Hence, the amount of heat developed in a conductor in a given time ( $t$ ) is equated thus:  $H=RI^2t$  or, in practice, Calories  $=0.239 \times \text{Ohms} \times (\text{Ampères})^2 \times \text{Seconds}$ .

**Kohlrausch** — Measurement of the conductivity of many salt and salt-like solutions is due to Kohlrausch's work (1876). These were measured at various concentrations and calculated to "infinite dilution." Taken with Hittorf's values for the rate of migration of ions the electrical conductance values (see Electrical Conductivity) are obtained.

**Ohm (Volt  $\div$  Ampère)** — The international unit of resistance is that offered by a column of mercury 106.3 centimetres in length, 14.4521 grams in mass, and at the temperature of melting ice, to an unvarying electric current.

**Rheostat** — An instrument for regulating the flow of electric currents, thus affording the means of controlling the amount according to Ohm's law which states that the amount ( $I$ ) of current is directly proportional to the electromotive force ( $E$ ) and inversely proportional to the resistance ( $R$ ) of the circuit ( $I=E/R$ ).

**Thermopile (Thermocouple)** — An apparatus constructed upon the knowledge that an electric current (which can be measured by a galvanometer) can be produced in a closed circuit by heating the point of contact of two dissimilar metals. The electromotive force (E.M.F.) of a bismuth-antimony pair when the junctions are kept at  $0^\circ$  and  $100^\circ$  C. is only 0.0115 volt, but using series of such pairs so arranged that the alternate junctions can be heated, the current is increased proportionally to the numbers of pairs. Various pairs of metals are used, for example, platinum *versus* platinum alloy, and "Alumel" *versus* "Chromel." (See Pyrometers.)

**Volt (Ampère  $\times$  Ohm)** —  $10^8$  absolute units is the electromotive force (E.M.F.) which, applied to a resistance of 1 ohm, produces a current of 1 ampère.

**Voltmeter** — An instrument for determining the intensity, potential, or electromotive force in terms of volts.

**Watt (Volt  $\times$  Ampère)** — The power of a direct electric current of 1 ampere flowing under a pressure of 1 volt, and approximately  $\frac{1}{746}$  part of 1 horse-power. (See *Elementary Lessons in Electricity and Magnetism*, by Silvanus Thompson (Macmillan and Co.); *Science in the Service of Man: Electricity*, by S. G. Starling (Longmans, Green and Co.); *Electricity and the Structure of Matter*, by L. Southern (Oxford Univ. Press).)

**ELECTROCHEMICAL SERIES** — See Electricity (Electromotive force).

**ELECTRODEPOSITION** — See Electricity.

**ELECTROMOTIVE SERIES** — See Electricity (Electromotive force).

**ELECTROOSMOSIS** — See Osmosis.

**ELECTROPLATING** — See Electricity.

**ELECTRODES** — See Carbon Electrodes, and Electricity.

**ELECTROLYSIS** — See Electricity.

**ELECTROLYTE** — See Electricity, and Electrolytic Dissociation.

**ELECTROLYTIC ALKALI PROCESS** — See Sodium and its compounds.

**ELECTROLYTIC CELLS** — See Electricity, Hydrogen, and Oxygen.

**ELECTROLYTIC DISSOCIATION** — Solutions of electrolytes, such as acids, bases, and salts, are made up of vast numbers of electrically charged particles (**ions**), part positively and an equal number negatively charged, by which the electrical current is conducted, and these polarities are designated in chemical symbols by a dot (·) or a plus sign (+) in association therewith in the case of **cations**, while **anions** are represented by an apostrophe (') or minus sign (−). The splitting up into cations and anions is variously termed electro-dissociation, ionic dissociation, and ionization. It is these charges of electricity which differentiate ions from the free elements. Aqueous solutions of sugar and urea are examples of non-electrolytes. (See S. Arrhenius on the "Theory of Electrolytic Dissociation" (Faraday Lecture, *J.C.S.*, 1914, 1414); *The Conductivity of Solutions and the Modern Dissociation Theory*, by C. W. Davies (Chapman and Hall, Ltd., London).)

The amount of a substance in a state of solution decomposed by an electric current is proportional to the amount of electricity, so that the same current passed through solutions of silver nitrate, copper sulphate, and gold trichloride causes the deposition of 108 grams of silver, 31·8 grams copper, and 65·7 grams gold, relatively, or absolutely by 96,500 coulombs of electricity. These quantities multiplied by their respective valencies (1, 2, 3, and 4) give their respective atomic weights, since gram equivalent weights require the same amount of electricity to deposit them.

Hittorf and Kohlrausch (see Electricity) measured the rate of migration of ions and the conductance of many solutions, respectively. Arrhenius (1887) assumed the degree of ionization equal to the ratio of conductance at a given dilution to that at infinite dilution. Debye and Hückel (1923) assumed complete ionization of highly conducting electrolytes to be complete at all dilutions and accounted for conductance changes by assuming each ion was surrounded by an "atmosphere" of oppositely charged ions dependent upon the dilution. Taken with Hittorf's values for the rate of migration of ions the electrical conductance values (see Electrical Conductivity) are obtained.

**ELECTRON** — A sub-atomic particle or corpuscle carrying a unit negative charge of electricity. Electrons exist in the free state as cathode rays and beta-particles. It is further predicated that every quantity of electricity is a multiple of this elementary charge. The mass of the atom of the lightest known element, namely, hydrogen, is 1,800 times the determined mass of the electron. From a chemical point of view, electrons must be constituent parts of atomic matter. The number of electrons in an atom is variously stated to be equal to the atomic number or approximately half its atomic weight, and the total internal energy of the electron has been given as about 500,000

volts. It was the view of Helmholtz that if elementary substances are composed of atoms, then electricity, positive as well as negative, must be divisible into definite elementary portions behaving like atoms, a view in accordance with Sir Joseph Thomson's original statement that electricity is possessed of mass and is atomic in structure. The passage of an electric current in a wire consists of the motion of electrons through the material composing the wire.

Certain experiments have been made which are regarded as being in support of the de Broglie wave theory, according to which the velocity and wave-length are governed by the speed and the mass of the particles.

If the electron is the unit of negative electricity and the proton that of positive electricity, then it follows that all the chemical elements, their compounds, and, indeed, the whole material universe, are composed of ponderable electricity. J. J. Thomson determined the charge on the electron, and in 1909 Robert A. Millikan measured the charge with notable accuracy.

The term electron is also used more generally to characterize the extremely minute particles shot off in electric discharges in gases, as well as the emissions from radioactive substances. (See *The Electron in Chemistry*, by J. J. Thomson (Chapman and Hall); *The Electron* by R. A. Millikan (Univ. of Chicago Press); *Ions, Electrons, and Ionizing Radiations*, by J. A. Crowther (Longmans, Green and Co.); *Electrons (+ and -) Protons, Photons, Neutrons, and Cosmic Rays*, by R. A. Millikan (Univ. of Chicago Press, 1935); *Atoms, Cathode Rays, Electricity, Elements, Energy, Matter, Nuclear Chemistry, Photons, Rays, and Radioactivity*.)

**ELECTRON COMPOUNDS** — Solid phases conforming to the Hume-Rothery rules (see same).

**ELECTRON VOLT** — The amount of energy acquired by an electron in falling through a potential difference of one volt. 1 electron volt =  $1.60 \times 10^{-12}$  erg. Nuclear reactions (see same) usually involve millions of electron volts (M.e.v.).

**ELECTROSCOPE** — An instrument for measuring radiation by means of the ionization produced. The ionization acts to discharge a condenser made of two parallel gold leaves or metal-coated quartz fibres, and the rate of discharge is observed.

**"ELEKTRON" (Metal)** — Alloys of magnesium with smaller quantities of other metals, used principally in construction of aeroplanes and motor-cars. (See *C.T.J.*, 88, 559 (1931).)

**ELEMENTS** — The chemical elements as generally understood are the various ultimate entities of matter of which all chemical substances are composed. F. Soddy has pointed out the difficulty of putting in few plain words a satisfactory definition of a chemical element. Perhaps the most common attitude of scientists is to consider that such an element is one that has been shown to occupy a definite place in the system resulting mainly from the work of Mendeléeff and of Moseley,

which topic is discussed later and which system is also displayed. Fundamentally, an element is characterized by atoms which contain the same number of protons in their nuclei.

Most of these chemical entities are metallic in character, but the non-metallic ones exist more abundantly in nature, and include oxygen, silicon, hydrogen, nitrogen, carbon, chlorine, bromine, fluorine, and iodine. (See Earth.) The two classes of metallic and non-metallic bodies gradually merge into one another, the intermediate class being sometimes described as metalloids—arsenic, for example.

The symbols used to represent the chemical elements are for the most part abbreviations of their common names; thus, the symbol of hydrogen is H, that of nitrogen N, that of calcium Ca; but there are exceptions, and while it is a pity that these exceptional symbols are still used, it will be useful to explain the reason. The metal antimony has the symbol Sb because the Latin name for antimony is *stibium*; lead has the symbol Pb, the Latin name for lead being *plumbum*; mercury is indicated by Hg, as the Latin name for it is *hydrargyrum*; potassium by K, its Latin name being *kalium*; sodium by Na, *natrium* being its Latin name; tin by Sn, from the Latin name *stannum*; gold by Au, from the Latin name *aurum*; iron by Fe, from the Latin name *ferrum*; silver by Ag, from the Latin name *argentum*; and copper as Cu, from the Latin name *cuprum*. (See Nomenclature.)

**Classification of the Elements**—The chief elements can, to some extent at least, be classified into groups in respect of certain resemblances as follows:

1. *Alkali metals*, including potassium, sodium, and lithium.
2. So-called *alkaline-earth* metals, including barium, strontium, calcium, and magnesium.
3. *Halogens*, including chlorine, bromine, iodine, and fluorine; so named because they form compounds with metals analogous to sodium chloride. By combination with hydrogen they form respectively hydrochloric, hydriodic, hydrobromic, and hydrofluoric acids (HCl, HI, HBr, and HF). (See Halides.)
4. Those better known in their gaseous state, including hydrogen, helium, chlorine, fluorine, oxygen, nitrogen, and argon.
5. The non-metals, including all the elements in classes 3 and 4, also boron, sulphur, carbon, phosphorus, and silicon.
6. Metals distinguished by (a) relatively low melting point: zinc, cadmium, mercury, aluminium, gallium, indium, thallium, tin, lead, antimony, bismuth; (b) marked ductility: iron, cobalt, nickel, the noble metals, molybdenum, tungsten, tantalum; and (c) brittleness: manganese, chromium, vanadium, titanium, zirconium.

Carbon is peculiar as being the one essential element of all so-called organic compounds, whilst silicon is one of the most abundant elements in the inorganic world, being a constituent of practically all rocks except pure limestone. Apart from the carbonates of the metals, most of the other compounds containing carbon are known as *organic* compounds, and, indeed, organic chemistry is sometimes defined as the chemistry of carbon and its compounds. These compounds are more numerous

K.C.E.—12

## ELEMENTS.

Arranged by

See Frontispiece for Arrangement

NOTE: Melting point data from U.S. National  
Atomic weight values in square brackets are for the

Element	Sym- bol	Atomic Number	Atomic Weight	Density at ° C. (Water= 1.000)	Melting Point, ° C.	Boiling Point, ° C.	Hard- ness	Atomic Radius, Å.U.	Electri- cal Con- ductivity (Cu= 100)	Specific Heat at ° C.
Actinium	Ac	89	227							
Aluminium	Al	13	26.97	2.702 20	660.0 ± 0.1	2057	2.9	1.43	64	0.217 17-100
Americium	Am	95	[241]							
Antimony	Sb	51	121.76	6.684 25	630.5 ± 0.1	1380	3.0	1.41	4	0.0503 20
Argon	A	18	39.944	1.402 -185.7	-189.4 ± 0.2	-185.7		1.91		0.125 15
Arsenic	As	33	74.91	$\alpha$ 5.73 14 $\beta$ 4.7 20 $\gamma$ 2.0	814 at 36 atm.	615 subl.	3.5	1.21	5	0.0822 0-100 (crys.)
Astatine	At	85	[210]							
Barium	Ba	56	137.36	3.5 20	704 ± 20	1140		2.17		0.068 -185 -+20
Berkelium	Bk	97								
Beryllium	Be	4	9.013	1.82 20	1280 ± 40	1500	3.0	1.12	9	0.425 0-100
Bismuth	Bi	83	209.00	9.80 20	271.3 ± 0.1	1450	1.8	1.51	1.5	0.0303 17-100
Boron	B	5	10.82	2.32 20	2040 ± 50	2550	9.5	0.89		0.25 0-100 -0.31 (crys.)
Bromine	Br	35	79.916	3.119 20	-7.2 ± 0.2	58.78		1.14		0.107 1-32 (liq.)
Cadmium	Cd	48	112.41	8.65 20	320.9 ± 0.1	770	2.0	1.49	23	0.0549 20
Calcium	Ca	20	40.08	1.55 20	850 ± 20	1240	1.5	1.97	37	0.149 0-100
Californium	Cf	98								
Carbon	C	6	12.010	Diam. 3.51 20 Graph. 2.25 20 Amor. 1.8-2.1	3700 ± 100	4200	Diam. 10.0 Graph. 1.0	0.77 Single bond 0.67 Double bond 0.60 Triple bond 0.70 Benzene bond	Graph. 0.2	Diam. 0.113 Graph. 0.160 Char. 0.165 0-24

## TABLE OF DATA

the Editor.

of the Elements and their Isotopes.

Bureau of Standards (10th April, 1947).

mass number of the most stable known isotope.

Heat of Fusion, Gm.-Cal./ Gm.	HEAT OF FORMATION Kilogram-Calories per Gram Formula Weight				Discoverer	Date	Element
	Chloride	Oxide	Sulphide	Hydride			
70.8	161.8 Al <sub>3</sub> Cl	399.0 2Al <sub>3</sub> O	344.8 2Al <sub>3</sub> S		Diebeene	1899	Actinium
					Giesel	1902	
					Wöhler	1827	Aluminium
38.2	91.4 Sb <sub>3</sub> Cl	166.9 2Sb <sub>3</sub> O	34.4 2Sb <sub>3</sub> S	34.3 Sb <sub>3</sub> H (gas)	Seaborg, James and Morgan	1945	Americium
					Thölden	1450	Antimony
6.71	43.5 As <sub>3</sub> Cl (liq.)	154.7 2As <sub>3</sub> O		-43.5 As <sub>3</sub> H (gas)	Rayleigh and Ram- say	1894	Argon
					Albertus Magnus	1250	Arsenic
					Corson, Mac Kenzie and Segré	1940	Astatine
	205.3 Ba <sub>2</sub> Cl	133.1 Ba <sub>2</sub> O	102.5 Ba <sub>2</sub> S	37.5 Ba <sub>2</sub> H	Davy	1808	Barium
					Thompson, Ghiorso and Seaborg	1949	Berkelium
					Vauquelin. Isolated by Wöhler and by Bussy	1797 1828	Beryllium
318	112.5 Be <sub>2</sub> Cl	136 Be <sub>2</sub> O			Geoffrey	1753	Bismuth
					Gay-Lussac and Thenard	1808	Boron
12.5	90.6 Bi <sub>3</sub> Cl	137.8 2Bi <sub>3</sub> O	75.8 2Bi <sub>3</sub> S		Davy	1808	
					Balard	1826	Bromine
16.2	0.70 Br <sub>2</sub> Cl (liq.)			8.7 H <sub>2</sub> Br (gas)	Stromeyer	1817	Cadmium
13.2	93.2 Cd <sub>2</sub> Cl	65.2 Cd <sub>2</sub> O	33.9 Cd <sub>2</sub> S		Davy	1808	Calcium
					Thompson, Ghiorso, Street and Seaborg	1950	Californium
	190.3 Ca <sub>2</sub> Cl	151.9 Ca <sub>2</sub> O	111.2 Ca <sub>2</sub> S	45.1 Ca <sub>2</sub> H	Pre-historic		Carbon
	33.2 C <sub>4</sub> Cl (liq.)	94.4 C <sub>2</sub> O (gas) 26.4 C <sub>2</sub> O (gas)	-19.0 C <sub>2</sub> S (liq.)	20.3 C <sub>4</sub> H (gas) -6.1 2C <sub>4</sub> H (gas) -54.3 2C <sub>2</sub> H (gas) -11.2 6C <sub>6</sub> H (liq.)			

Element	Sym- bol	Atomic Number	Atomic Weight	Density at ° C. (Water= 1.000)	Melting Point, ° C.	Boiling Point, ° C.	Hard- ness	Atomic Radius, Å.U.	Electri- cal Con- ductivity (Cu= 100)	Specific Heat at ° C.
Cerium	Ce	58	140.13	Cub. 6.9 20 Hex. 6.7	600 ± 50	1400	2.5	1.81	2	0.0448 0-100
Cesium	Cs	55	132.91	1.90 20	28 ± 2	670	0.2	2.62	8	0.048 0-26
Chlorine	Cl	17	35.457	1.56 -34.6	-101 ± 2	-34.6		0.99		0.226 (liq.) 0-24
Chromium	Cr	24	52.01	6.92 20	1800 ± 50	2200	9.0	1.25	65	0.110 17-100
Cobalt	Co	27	58.94	8.9 20	1495 ± 1	2900	5.0	1.25	17	0.1041 0-100
Columbium See Niobium	Cb									
Copper	Cu	29	63.54	8.92 20	1083.2 ± 0.1	2310	3.0	1.28	100	0.0912 20
Curium	Cm	96	[242]							
Deuterium. See Hydrogen										
Dysprosium	Dy	66	162.46							
Erbium	Er	68	167.2	4.77 15						
Europium	Eu	63	152.0							
Fluorine	F	9	19.00	1.11 -187	-223	-187		0.64		
Francium	Fr	87	[223]							
Gadolinium	Gd	64	156.9							
Gallium	Ga	31	69.72	5.885 24	29.78 ± 0.02	1700	1.5	1.24	5	0.079 12-23
Germanium	Ge	32	72.60	5.36 20	958 ± 10	2700	6.2	1.22		0.074 0-100
Glucinum. See Beryllium	Gl									
Gold	Au	79	197.2	19.3 20	1063.0 ± 0.0	2600	2.5	1.44	70	0.0316 0-100
Hafnium	Hf	72	178.6	13.3 20	1700	>3200				
Helium	He	2	4.003	0.147 -268.9	-271.4 ± 0.2 at 30 atm	-268.9		0.53		1.25 -180
Holmium	Ho	67	164.94							

Heat of Fusion, Gm.-Cal./ Gm.	HEAT OF FORMATION Kilogram-Calories per Gram Formula Weight				Discoverer	Date	Element
	Chloride	Oxide	Sulphide	Hydride			
	234.9 Ce,2O				Klaproth ; Berzelius and Hisinger Isolated by Hille- brand and Norton	1803 1895	Cerium
3.8	106.4 Ca,Cl	82.7 2Ca,O			Bunsen and Kirchhoff	1860	Cesium
23.0		-17.9 2Cl,O (gas)		22.0 H,Cl (gas)	Isolated by Scheele, but believed to be a compound Named an element by Davy	1774 1810	Chlorine
31.7		267.8 2Cr,3O			Vauquelin	1797	Chromium
58.3	76.5 Co,2Cl	57.5 Co,O 193.4 3Co,4O	19.7 Co,S (ppt.)		Brandt	1735	Cobalt
43.2	51.6 Cu,2Cl	34.9 Cu,O 40.8 2Cu,O	11.6 Cu,S		Pre-historic		Copper
					Seaborg, James and Ghiorso	1944	Curium
					de Boisbaudran	1886	Dysprosium
					Mosander	1843	Erbium
					Demarcay	1901	Europium
10.1					Moissan	1886	Fluorine
					Mlle. M. Perey	1940	Francium
					Marignac	1880	Gadolinium
19.0					de Boisbaudran	1875	Gallium
					Winkler	1886	Germanium
16.1	27.0 Au,3Cl	-12.3 2Au,3O			Pre-historic		Gold
					Coster and von Hevesy Isolated by van Arkel and de Boer	1923 1925	Hafnium
					In the sun by Lock- yer Isolated by Ramsay	1868 1895	Helium
					Cleve	1879	Holmium

Element	Sym- bol	Atomic Number	Atomic Weight	Density at ° C. (Water = 1.000)	Melting Point, ° C.	Boiling Point, ° C.	Hard- ness	Atomic Radius, Å.U.	Electri- cal Con- ductivity (Cu = 100)	Specific Heat at ° C.
Hydrogen	H	1	1.0080	0.0709 -252.7	-259.2 ± 0.1	-252.7		0.28		3.4 15
Deuterium	D	1	2.016		-254.5 ± 0.2	-249.7				
Indium	In	49	114.76	7.3 20	156.4 ± 0.1	1450	1.2		19	0.0323 18-100
Iodine	I	53	126.92	4.93 20	114 ± 1	184.35	0.8	1.33		0.054 9-98
Iridium	Ir	77	193.1	22.4 20	2454 ± 3	>4800	6.5	1.35	28	0.1065 20
Iron	Fe	26	55.85	7.86 20 7.83 (C,1%) 7.60 (C,3%)	1539 ± 3 1430 (C,1%) 1150 (C,3%)	3000	4.0	1.27	17	0.1065 20
Krypton	Kr	36	83.7	2.155 -151.8	-157.0 ± 0.5	-151.8		1.98		
Lanthanum	La	57	138.92	6.15 20	826 ± 5	1800		1.86	3	0.0448 0-100
Lead	Pb	82	207.21	11.337 20	327.4 ± 0.1	1620	1.5	1.46	8	0.0305 20-100
Lithium	Li	3	6.940	0.53 20	186 ± 5	1336 ± 5, 1609 ± 5	0.6	1.50	18	1.09 0-100
Lutetium	Lu	71	174.99							
Magnesium	Mg	12	24.32	1.74 20	650 ± 2	1110	2.6	1.60	38	0.248 17-100
Manganese	Mn	25	54.93	7.2 20	1260 ± 20	1900	6.0	1.18	34	0.1072 0
Mercury	Hg	80	200.61	13.546 20	-38.87 ± 0.02	356.9		1.50	1.7	0.03325 20
Molybdenum	Mo	42	95.95	10.2 20	2625 ± 50	3700	6.0	1.36	30	0.072 15-93
Neodymium	Nd	60	144.27	6.9 20	840 ± 40				2	
Neon	Ne	10	20.183	1.204 -245.9	-248.6 ± 0.3	-245.9		1.60		
Neptunium	Np	93	[237]							
Nickel	Ni	28	58.69	8.90 20	1455 ± 1	2900	5.0	1.24	22	0.1089 15-100
Niobium	Nb	41	92.91	8.4 20	2500 ± 50	>3300				

Heat of Fusion, Gm.-Cal./ Gm.	HEAT OF FORMATION Kilogram-Calories per Gram Formula Weight				Discoverer	Date	Element
	Chloride	Oxide	Sulphide	Hydride			
14.0	22.0 H,Cl (gas)	68.4 2H <sub>2</sub> O (liq.) 44.5 2H <sub>2</sub> O (liq.)	5.3 2H <sub>2</sub> S (gas)		Cavendish	1766	Hydrogen
					Urey	1932	Deuterium
					Reich and Richter	1863	Indium
15.8	4.5 I,Cl (liq.)	42.1 2I,SO		— 5.9 H,I (gas)	Courtois	1811	Iodine
					Tennant	1803	Iridium
48.0	96.0 Fe <sub>3</sub> Cl	65.7 Fe <sub>2</sub> O 265.2 3Fe <sub>2</sub> O	23.1 Fe <sub>2</sub> S		Pre-historic		Iron
4.3					Ramsay and Travers	1898	Krypton
	266.7 La <sub>2</sub> Cl	456.9 2La <sub>2</sub> SO	317.3 2La <sub>2</sub> SO		Mosander	1839	Lanthanum
5.42	83.9 Pb <sub>2</sub> Cl	52.5 Pb <sub>2</sub> O 174.2 3Pb <sub>2</sub> O	22.2 Pb <sub>2</sub> S (ppt.)		Pre-historic		Lead
120	97.0 Li,Cl	141.7 2Li <sub>2</sub> O		21.6 Li <sub>2</sub> H	Arfvedson	1817	Lithium
					Urbain	1907	Lutetium
70.1	153.2 Mg <sub>2</sub> Cl	143.9 Mg <sub>2</sub> O	82.2 Mg <sub>2</sub> S		Davy	1808	Magnesium
36.5	112.0 Mn <sub>2</sub> Cl	90.8 Mn <sub>2</sub> O 324.9 3Mn <sub>2</sub> O	47.3 Mn <sub>2</sub> S (ppt.)		Gahn	1774	Manganese
2.77	53.3 Hg <sub>2</sub> Cl 31.3 Hg <sub>2</sub> Cl	21.7 Hg <sub>2</sub> O	10.6 Hg <sub>2</sub> S (ppt.)		Pre-historic		Mercury
		174.0 Mo <sub>2</sub> SO			Hjelm	1781	Molybdenum
	249.5 Nd <sub>2</sub> Cl	435.1 2Nd <sub>2</sub> SO	262.6 2Nd <sub>2</sub> SO		von Welsbach	1885	Neodymium
2.6					Ramsay and Travers	1898	Neon
					McMillan and Abelson	1940	Neptunium
73.9	74.5 Ni <sub>2</sub> Cl	57.9 Ni <sub>2</sub> O	17.4 Ni <sub>2</sub> S (ppt.)		Cronstedt	1751	Nickel
					Hatchett Isolated Blomstrand	1801 1864	Niobium

Element	Sym- bol	Atomic Number	Atomic Weight	Density at ° C. (Water= 1 000)	Melting Point, ° C.	Boiling Point, ° C.	Hard- ness	Atomic Radius, ° Å. U.	Electri- cal Con- ductivity (Cu= 100)	Specific Heat at ° C.
Nitrogen	N	7	14.008	0.808 -195.8	-210.0 ± 0.1	-195.8		0.70 Single bond 0.63 Double bond 0.55 Triple bond		0.0284 -208 - -196
Osmium	Os	76	190.2	22.48 20	2700 ± 200	>5300	7.0	1.34	19	0.0311 19-98
Oxygen	O	8	16.0000	1.14 -183	-218.8 ± 0.1	-183.0		0.66 Single bond 0.59 Double bond		0.35 -200 - -183
Palladium	Pd	46	106.7	12.0 20	1554 ± 1	2200	4.0	1.37	16	0.0592 0-100
Phosphorus	P	15	30.98	Yellow 1.82 20 Red 2.20 20 Black 2.69	Yellow 44.1 ± 0.1 Red 590 at 43 atm.	280	Yellow 0.5	1.10		Yellow 0.190 7-30 Red 0.183 0-51
Platinum	Pt	78	195.23	21.45 20	1773.5 ± 1	4300	4.3	1.38	16	0.03224 15-100
Plutonium	Pu	94	[239]							
Polonium	Po	84	210							
Potassium	K	19	39.096	0.86 20	63 ± 1	760	0.5	2.31	24	0.188 0-22
Praseodymium	Pr	59	140.92	6.5 20	940 ± 50				2	
Promethium	Pm	61	[147]							
Protactinium	Pa	91	231		3000					
Radium	Ra	88	226.05	5	700	1140				
Radon	Rn	86	222	4.4 -62	-71	-61.8				
Rhenium	Re	75	186.31	20.53	3170 ± 60				8	
Rhodium	Rh	45	102.91	12.5	1966 ± 3	>2500	6.0	1.34	33	0.0580 10-57
Rubidium	Rb	37	85.48	1.53 20	39 ± 1	700	0.3	2.44	14	0.0802 0
Ruthenium	Ru	44	101.7	8.6	2500 ± 100		7.5	1.32	17	0.061 0-100

Heat of Fusion, Gm.-Cal./ Gm.	HEAT OF FORMATION Kilogram-Calories per Gram Formula Weight				Discoverer	Date	Element
	Chloride	Oxide	Sulphide	Hydride			
6.09		-21.6 N <sub>2</sub> O (gas) -2.7 2N <sub>2</sub> O (gas)	-31.9 N <sub>2</sub> S	10.9 N <sub>2</sub> H <sub>4</sub> (gas)	Rutherford	1772	Nitrogen
3.30					Tennant	1803	Osmium
					Priestley	1774	Oxygen
36	43.5 Pd <sub>2</sub> Cl			17.7 2Pd <sub>2</sub> H	Wollaston	1803	Palladium
5.03	76.6 P <sub>2</sub> Cl <sub>3</sub> (liq.)	365.2 2P <sub>2</sub> O		-6.0 P <sub>2</sub> H <sub>4</sub> (gas)	Brand	1669	Phosphorus
27	62.6 Pt <sub>2</sub> Cl	17.0 Pt <sub>2</sub> O			Wood	1741	Platinum
					Seaborg, McMillan, Kennedy and Wahl	1940	Plutonium
					Mme Curie	1898	Polonium
14.5	104.3 K <sub>2</sub> Cl	86.3 2K <sub>2</sub> O	87.1 2K <sub>2</sub> S	14.1 K <sub>2</sub> H	Davy	1807	Potassium
	240.4 Pr <sub>2</sub> Cl	215.1 Pr <sub>2</sub> O			von Welsbach	1885	Praseodymium
					Glendenin and Marinsky	1945	Promethium
					Hahn and Meitner Soddy and Cranston Isolated by von Grosse	1917 1918 1934	Protactinium
					Marie and Pierre Curie Isolated by Marie Curie and Debierne	1898 1910	Radium
					Explained by Dorn	1900	Radon
					Noddack, Tacke, and Berg	1924	Rhenium
					Wollaston	1803	Rhodium
6.10	105.0 Rb <sub>2</sub> Cl	83.5 2Rb <sub>2</sub> O	87.7 2Rb <sub>2</sub> S		Bunsen and Kirchhoff	1861	Rubidium
					Claus	1844	Ruthenium

Element	Sym- bol	Atomic Number	Atomic Weight	Density at ° C (Water = 1.000)	Melting Point, ° C	Boiling Point, ° C	Hard- ness	Atomic Radius, Å, U.	Electri- cal Con- ductivity (Cu = 100)	Specific Heat at ° C.
Samarium	Sm	62	150.43	7.7	>1300					
Scandium	Sc	21	45.10	2.5	1200	2400				
Selenium	Se	34	78.96	Crys. grey 4.79 Crys. red 4.46 Amor. red 4.26	Crys. grey 220 ± 5 Crys. red 170-180	688	2.0	1.17	14	0.084 22-63 (crys.)
Silicon	Si	14	28.06	Crys. 2.4 20 Graph. 2.0-2.5 Amor. 2	1415 ± 20	2600	Crys. 6.5	1.17	3	0.170 21 (Crys.)
Silver	Ag	47	107.880	10.5 20	960.5 ± 0.0	1950	2.7	1.44	104	0.05625 15-100
Sodium	Na	11	22.997	0.97 20	97.7 ± 0.2	880	0.4	1.84	37	0.290 27
Strontium	Sr	38	87.63	2.6	770 ± 10	1150	1.8	2.15	7	
Sulphur	S	16	32.066	Rhom. 2.07 Monocl. 1.96	Rhom. 112.8 ± 0.2 Monocl. 119.2 ± 0.2	444.6	Rhom. 2.0	1.04		Rhombic 0.1728 0-54 Monoclinic 0.1809 0-52
Tantalum	Ta	73	180.88	16.6	3000 ± 100	>4100	7.0		11	0.036 58
Technetium	Tc	43	[99]							
Tellurium	Te	52	127.61	α 6.24 β 6.00	450 ± 10	1390	2.3	1.37		0.0483 15-100 (Crys.)
Terbium	Tb	65	159.2		327 ± 5					
Thallium	Tl	81	204.39	11.85	300 ± 3	1457	1.2		9	0.0326 20-100
Thorium	Th	90	232.12	11.2	1800 ± 150	>3000			9	0.0276 0-100
Thulium	Tm	69	169.4							
Tin	Sn	50	118.70	Tetrag. 7.31 Rhom. 6.55 Grey, cub 5.75	231.9 ± 0.1	2260	1.8	1.40	15	0.0541 -20
Titanium	Ti	22	47.90	4.50 17.5	1820 ± 100	>3000	4.0	1.45	56	0.1125 0-100
Tungsten, See Wolfram										
Uranium	U	92	238.07	18.49 13	1133 ± 3	3500			3	0.028 0-98

Heat of Fusion. Gm.-Cal./ Gm.	HEAT OF FORMATION Kilogram-Calories per Gram Formula Weight				Discoverer	Date	Element
	Chloride	Oxide	Sulphide	Hydride			
Grey 6·7	22·2 2Se,2Cl (liq.)	57·1 Se <sub>2</sub> O		—15·8 Se,2H (gas)	de Boisbaudran	1879	Samarium
					Nilson Isolated by Fischer, Brünger & Grieneisen	1879 1937	Scandium
					Berzelius	1817	Selenium
	149·1 Si,4Cl (liq.)	201·4 Si <sub>2</sub> O	32·0 Si <sub>2</sub> S	11·9 Si,4H (gas)	Berzelius	1823	Silicon
15·1	30·6 Ag,Cl	7·0 2Ag <sub>2</sub> O	5·0 2Ag <sub>2</sub> S		Pre-historic		Silver
27·5	98·4 Na,Cl	99·2 2Na <sub>2</sub> O	89·7 2Na <sub>2</sub> S	13·1 Na <sub>2</sub> H	Davy	1807	Sodium
	197·9 Sr,2Cl	140·7 Sr <sub>2</sub> O	110·3 Sr <sub>2</sub> S	42·1 Sr,2H	Davy	1808	Strontium
Rhom. 9·37 Monocl. 10·4	14·3 2S,2Cl (liq.)	69·3 S <sub>2</sub> O (gas) 91·5 S <sub>3</sub> O (gas)		5·3 S,2H (gas)	Pre-historic		Sulphur
		300·1 2Ta <sub>2</sub> O <sub>5</sub>			Ekeberg	1802	Tantalum
	77·4 Te,4Cl	78·3 Te <sub>2</sub> O		—33·9 Te,2H (gas)	Perrier and Segrè	1937	Technetium
					Isolated by Muller but not named Named by Klaproth	1782 1798	Tellurium
					Mosander	1843	Terbium
7·20	48·7 Ti,Cl	42·2 2Ti <sub>2</sub> O	22·0 2Ti <sub>2</sub> S		Crookes	1861	Thallium
	335·0 Th,4Cl	330·9 Th <sub>2</sub> O		—42·8 Th <sub>2</sub> H	Berzelius	1828	Thorium
14	127·4 Sn,4Cl (liq.)	138·1 Sn <sub>2</sub> O	23·9 Sn <sub>2</sub> S		Cleve	1879	Thulium
					Pre-historic		Tin
	183·5 Ti,4Cl (liq.)	218·4 Ti <sub>2</sub> O			Gregor Isolated by Hunter	1791 1910	Titanium
		290·1 U <sub>3</sub> O			Klaproth Isolated by Peligot	1789 1841	Uranium

Element	Sym- bol	Atomic Number	Atomic Weight	Density at °C. (Water = 1.000)	Melting Point, °C.	Boiling Point, °C.	Hard- ness	Atomic Radius, Å.U.	Electri- cal Con- ductivity (Cu = 100)	Specific Heat at °C.
Vanadium	V	23	50.95	5.96	1735 ± 50	3000		1.30		0.1153 0-100
Wolfram	W	74	183.92	19.3	3410 ± 20		7.0	1.37	31	0.034 20-100
Xenon	Xe	54	131.3	3.06 - 109.1	- 112 ± 1	- 107.1		2.18		
Ytterbium	Yb	70	173.04		1800					
Yttrium	Y	39	88.92	5.51	1490 ± 200	2500				
Zinc	Zn	30	65.38	7.14	419.5 ± 0.1	907	2.5	1.32	28	0.0924 20
Zirconium	Zr	40	91.22	6.4	1750 ± 700	>2900	4.5	1.58		0.068 0-100

than those of all the other elements, and so far as they are constituents of animal and vegetable tissues, they are of more complicated constitution than most other chemical compounds: in addition to carbon, oxygen, and hydrogen, they not infrequently include nitrogen, sulphur, and phosphorus as constituents. (See Chemical Compounds.)

**Periodic Law (See Frontispiece for Arrangement of the Chemical Elements)**—Many of the chemical elements that, to some extent, resemble one another in their properties appear also to exhibit certain numerical relations—for example, lithium and potassium, having the atomic weights of 7 and 39, exhibit an average number 23, which is the atomic weight of sodium. These and other numerical relations and the gradations in the properties of such elements have led up to what is known as the periodic law, the basic idea being that the chemically analogous elements constitute families, the members of which recur after regular intervals when arranged in order of their atomic weights. It may be broadly expressed by the statement that the properties of the elements and their compounds constitute a periodic function of their elemental atomic weights. These functions are noticeable, for example, in their electrical characters, the ductility, malleability, and melting-points of the metals; in their so-called atomic volumes, and the atomic heats of the elements; and the compressibilities of the solid elements as determined by T. W. Richards, of Harvard University, each and all as periodic functions of their atomic weights.

Moseley (1914), by using different metals as the target in an X-ray tube, a crystal-reflection grating to deflect the radiation, and an electroscope for recording this radiation, determined the wave lengths of the characteristic X-rays emitted by each metal (element). He found that a simple numerical relationship exists between each succeeding element and the frequencies (the number of wave lengths per unit of time) of the corresponding lines of their X-ray spectra. The

Heat of Fusion, Gm.-Cal./ Gm.	HEAT OF FORMATION Kilogram-Calories per Gram Formula Weight				Discoverer	Date	Element
	Chloride	Oxide	Sulphide	Hydride			
3.77	187.1 V <sub>2</sub> O <sub>5</sub> (liq.)	437.3 2V <sub>2</sub> O <sub>5</sub>			Solstrom Isolated by Roscoe	1830 1869	Vanadium
		191.4 W <sub>2</sub> O <sub>3</sub>			d'Elhujar Brothers	1783	Wolfram
					Ramsay and Travers	1898	Xenon
					Marignac	1878	Ytterbium
26.1	99.5 Zn <sub>2</sub> Cl <sub>2</sub>	85.0 ZnO	41.3 ZnS (ppt.)		Gadolin	1794	Yttrium
		178.7 Zr <sub>2</sub> O <sub>3</sub>			Marggraff	1746	Zinc
					Klaproth	1789	Zirconium

square root of the frequency is practically a straight line function of the position of the elements in the periodic arrangement. The *atomic number*, used to locate this position, is a fundamental constant of nature, and is equal to the positive charge on the nucleus of the atom, which is also the same number as the electrons surrounding this nucleus (the atom being electronically neutral). This discovery has been of great significance, for example, (1) elements that were out of order in the atomic weight arrangement (tellurium and iodine, cobalt and nickel, argon and potassium) fall into their proper places using atomic number arrangement, and (2) the number of rare earth elements, so similar chemically, is definitely shown. In nature it appears that the elements of even atomic number are much more abundant than those of odd atomic number, and the even-numbered radioactive elements have longer lives than the odd-numbered.

Caven and Lander remark that "the periodic law still affords the

#### ELECTRON ARRANGEMENT IN THE ATOMS OF THE NOBLE GASES

Last Element in the Series (and its atomic weight)	Atomic Number	Number of Elements in the Preceding Series (Note)	Number of Electrons to Complete						Level of Successive Shells
			1st	2nd	3rd	4th	5th	6th	
Helium (4)	2	2	2	—	—	—	—	—	
Neon (20)	10	8	2	8	—	—	—	—	
Argon (40)	18	8	2	8	8	—	—	—	
Krypton (84)	36	18	2	8	18	8	—	—	
Xenon (131)	54	18	2	8	18	18	8	—	
Radon (222)	86	32	2	8	18	32	18	8	

Note: Unit change of electrons from element to element in each series.

most complete method of systematic classification," and Grosse in *Science*, December 7, 1934, 512, states his opinion that it is "the greatest generalization of chemistry in the last century." (See John A. R. Newlands on *The Periodic Law* (E. and F. N. Spon, London); D. Mendeléeff on "Periodic Law of the Chemical Elements" (Faraday Lecture, Chem. Soc., 1889); Tilden's "Mendeléeff Memorial Lecture" (Chem. Soc., 1909); *The Periodic Law*, by F. P. Venable; *The Periodic Law*, by A. E. Garrett; *Systematic Inorganic Chemistry: from the Standpoint of the Periodic Law*, by Caven and Lander (Blackie and Son, London); Chapter I. *The Chemical Elements*, of Morgan and Burstall's *Inorganic Chemistry, a Survey of Modern Developments*, 1936 (Heffer, Cambridge); *The Chemical Elements and Their Compounds*, by N. V. Sidgwick, 1950 (Oxford Univ. Press). (See Atoms, Electrons, Isotopes, Matter, and Radioactivity.)

A list of the chemical elements is given in the accompanying table, and most of their chief compounds are described in this work under their several names. The First Report of the Committee on Atomic Weights of the International Union of Chemistry, giving the results of investigations published since January 1, 1930, appeared in *J. Amer. Chem. Soc.*, **53**, 1627 (1931), and since then reports appear annually in the same journal and in *J.C.S.* The International Union of Chemistry, in 1949, took action on several elements, the results of which are shown under the respective elements, for example, plutonium.

**ELEMI** — See Gums and Resins.

**ELEOPTENES** — See Stearoptenes.

**"ELINVAR"** — An alloy used for the manufacture of the balance springs of watches. Its coefficient of elasticity does not change with the temperature, so that the control of the spring does not vary with the temperature.

**"ELITONE"** — See Nikethamide.

**ELUTRIATION** — A method of separating smaller particles from larger, or less dense particles from more dense, by suspending a powdered solid in an upward current of fluid. The velocity of the current is adjusted so that the smaller or less dense particles are carried up with the fluid while the larger or more dense particles sink against the current. The fluid may be either liquid or gaseous, and the operation may be conducted batch-wise or continuously.

A common type of elutriator consists of a conical-bottomed vessel having a liquid inlet near the bottom. The material to be treated is introduced through a pipe into the centre of the vessel. Large or heavy particles sink to the apex of the cone and are discharged through a star valve or similar device; fine or light particles overflow the rim of the vessel together with the liquid and are collected in an annular trough.

Elutriation with water is used in coal washing to separate coal from the denser shale and dirt. Air elutriation is embodied in some fine-grinding systems, oversize particles being returned to the mill. Elutriation is employed in the laboratory to determine the size distribution of finely divided materials such as soils, clays, and pigments.

“**ELVACET**” (Du Pont) — Trade-name for thermoplastic polyvinyl acetates. Used as adhesives, binders, protective coatings, and grease-proofers.

“**ELVALOL**” (Du Pont) — Trade-name for polyvinyl alcohols, water-soluble synthetic resins, odourless, tasteless, and non-toxic. The films produced are highly impermeable to air and gases, and unaffected by oils, fats, greases, hydrocarbons, and many organic solvents. The films are used as adhesives and binders for paper, cloth, and leather, and as top size on paperboard for high-gloss printing.

**EMANATIONS** — Waves or electronic or gaseous products radiated or evolved from substances. (See Elements, Helium, Radioactivity, Radiation, and Radium.)

**EMBOLITE** — A mineral chlorobromide of silver (of crystal system No. 1, and sp. gr. 5.79) found in Arizona, Colorado, New Mexico, and Chile, having the composition variously given as  $\text{Ag}_5\text{Cl}_3\text{Br}_2$  and  $\text{Ag}(\text{ClBr})$ .

**EMERALD** — A gem found in mineral form in Colombia, Venezuela, etc., being a double silicate of aluminium and beryllium, or green variety of *beryl*, containing some chromium sesquioxide ( $\text{Cr}_2\text{O}_3$ ).

**EMERALD GREEN** — See Copper Compounds.

**EMERY** — See Abrasives, and Aluminium (Corundum).

**EMETINE** ( $\text{C}_{29}\text{H}_{40}\text{O}_4\text{N}_2$ ) — An alkaloid obtained from ipecacuanha root or prepared by methylation of cephaeline. It is used in medicine in the form of its hydrochloride,  $\text{C}_{29}\text{H}_{40}\text{O}_4\text{N}_2 \cdot 2\text{HCl} \cdot 7\text{H}_2\text{O}$ , for the treatment of amœbic dysentery. For oral administration it has also been used as a complex iodide prepared by precipitation from a solution of emetine hydrochloride by the addition of potassium bismuth iodide solution. (See Ipecacuanha.)

**EMODIN** ( $\text{C}_{40}\text{H}_{30}\text{O}_{13}$ ) — A crystalline, orange-coloured derivative of anthraquinone, m.p.  $250^\circ\text{C}$ ., soluble in alcohol. Found as a constituent of rhubarb root and cascara bark and other purgative drugs.

“**EMPIWAX**” — See Waxes (Emulsifying Wax).

**EMULSIN** (*Synaptase*) — An enzyme or a mixture of enzymes occurring in sweet and bitter almonds, capable of hydrolysing  $\beta$ -glucosides but without action on  $\alpha$ -glucosides.

**EMULSIONS** — When kerosene and water are placed in the same container they will separate into two layers with kerosene on top and the water on the bottom due to their mutual immiscibility and the difference in densities. But when the liquids are violently shaken a turbid mixture is formed which quickly separates into two layers when the shaking is stopped. If a small amount of a third substance, called an emulsifying agent, is added to the kerosene and water and the mixture again agitated violently, a milky fluid which is apparently uniform is formed which does not separate when the shaking is stopped. This milky liquid which is an intimate mixture of two immiscible liquids is called an emulsion.

While the emulsion looks uniform to the naked eye a microscopic examination shows a definite non-uniformity consisting of a multitude of small globules floating around in a liquid medium. In order to discuss emulsions we must distinguish between the two phases of an emulsion. The separate globules—the discontinuous phase—consist entirely of one of the liquids—also called the internal phase because it appears to be inside the liquid medium. On the other hand, the liquid medium—the continuous phase—is called the external phase. Since most emulsions consist of an aqueous layer and an “oil-like” layer the two phases are often referred to as the water phase and the oil phase. For example, resins, waxes, hydrocarbons, nitrocellulose solutions are “oil-like” when in water. Depending upon a number of conditions the water phase may be either the internal or the external phase. Thus the emulsifying agent, the ratio of the water phase to oil phase, the method of mixing, etc., are factors which determine whether water is the internal or the external phase of an emulsion.

If the oil phase is the internal phase we have an oil-in-water type emulsion, conventionally labelled O/W emulsion. Conversely, if the water phase is the internal phase we have a water-in-oil emulsion, labelled W/O emulsion.

When two emulsions are made up of the same two components in approximately the same ratio, say 50 per cent. oil phase to 50 per cent. water phase, so that one is a W/O emulsion and the other is an O/W emulsion it is surprising to find that the two phases have quite different properties although they may look alike to the naked eye. For example, the O/W emulsion behaves as a water system: it can be diluted with water but not with the oil-like component; it will conduct the electric current in the presence of an electrolyte since there is a continuous water solution present; it will become coloured by water-soluble dyes but not by oil-soluble dyes. Conversely, the W/O emulsion cannot be diluted by water but only by the oil-like phase; it will not readily conduct the electric current; it will become coloured not by water-soluble but by oil-soluble dyes because it is an oil-like solution.

The particle size of the emulsion droplets which compose the internal phase is an important criterion in defining and understanding the behaviour of emulsions. The maximum diameter of emulsions is about  $25\mu$  ( $0.025$  mm.) while the minimum value is about  $0.25\mu$  ( $0.00025$  mm.), and generally the emulsion diameters vary between  $1\mu$  ( $0.001$  mm.) and  $10\mu$  ( $0.01$  mm.). Take 1 ml. of water and 1 ml. of an oil, add a small amount of an emulsifying agent, and shake until an emulsion is formed (occupying 2 ml.), the droplets having a diameter of  $5\mu$  ( $0.005$  mm.) for the internal phase. How many droplets will there be? What will be the surface area of these droplets? Before emulsification each phase had a surface area of about  $6\text{ cm.}^2$  The volume of a droplet having a diameter of  $5\mu$  is  $64.5 \times 10^{-12}\text{ cm.}^3$  The number of such droplets in 1 ml. will be  $1.54 \times 10^{10}$  or 15,400,000,000. The surface area of one droplet having a diameter of  $5\mu$  will be  $77.5 \times 10^{-8}\text{ cm.}^2$  The total area of all the droplets will be  $12,000\text{ cm.}^2$  Thus in the 2 ml. of emulsion we have 15,400,000,000 droplets, each in contact with

the external phase forming an interface of 12,000 cm.<sup>2</sup> or about 1,850 in.<sup>2</sup> Any phenomenon that depends upon surface area, such as adsorption or surface tension, will be greatly magnified in an emulsion over what it would show in non-emulsion solution.

To understand the size relation between an emulsion internal phase droplet and a molecule consider water broken up into droplets of diameter  $1\mu$  (0.001 mm.). The volume of such a droplet is  $5.2 \times 10^{-13}$  cm.<sup>3</sup>, while the volume of a molecule of water is  $3 \times 10^{-23}$  cm.<sup>3</sup> Therefore  $5.2 \times 10^{-13}$  cm.<sup>3</sup> divided by  $3 \times 10^{-23}$  cm.<sup>3</sup> yields  $1.7 \times 10^{10}$  or 17,000,000,000 molecules in one water droplet of  $1\mu$  diameter.

In the original experiment of mixing water and kerosene the two immiscible liquids did not emulsify because each has a large interfacial tension tending to decrease its surface area thus strongly opposing the conditions necessary to give a large surface area as indicated above. That is to say the normal tendency of water due to its high interfacial tension is to have particles coalesce to decrease its surface area as much as possible, and similarly the high interfacial tension of kerosene will cause it to coalesce and decrease its surface area. In order to have water and kerosene form an emulsion the interfacial tension must be reduced. This is the function of the emulsifying agent

An emulsifying agent should meet the following requirements: (1) It must reduce the interfacial tension. (2) It must stabilize the emulsion. (3) It must be chemically stable. (4) It should be selective. (5) It should be fairly odourless, light in colour, and cheap. (6) It should meet special requirements in special cases.

Emulsifying agents act by positive adsorption, by polarity, and by orientation. The properties of a water-oil interfacial film produced by a soap-like emulsifying agent would be a typical example: Soap (RCOONa) can be thought of as a long molecule having dissimilar ends. The R- end is oil-like, the carboxyl (-COONa) end is water soluble, the soap molecules orient themselves at the interface and cause a decrease in the interfacial tension, thus allowing the interfacial area to be increased.

The following is a list of various emulsifying agents:

(1) Soaps. Sodium salts of the fatty acids having 12 or more carbon atoms in the chain, such as lauric, palmitic, stearic, linoleic, and oleic.

(2) Organic amino-compounds producing soaps with fatty acids. Some of these amino-compounds are *n*-methylmorpholine, ethylenediamine, propylenediamine, morpholine, dimethylaminoethanol, *n*-ethylmorpholine, diethylaminoethanol, 2-amino-2-methylpropanol-1, monoethanolamine, 2-aminobutanol-1, diethanolamine, triethanolamine, and 2-amino-2-methylpropanediol-1,3.

(3) Sulphated compounds. Sulphated oils, such as Turkey-red oil, and sulphated alcohols, such as sodium lauryl sulphate, sodium cetyl sulphate, and sodium monolauryl glyceryl sulphate.

(4) Sulphonated agents, such as dioctyl sodium sulphosuccinate, isopropyl naphthalene sodium sulphonate, dodecyl benzene sodium sulphonate, and sulphonaphthyl stearic acid.

(5) Cation-active agents, such as cetyl dimethyl benzyl ammonium chloride, diethyl aminoethyl oleylamide acetate, and lauryl pyridinium iodide.

(6) Non-ionic agents, such as glycol, glycerol, hexitol, and diethylene glycol.

(7) Natural agents, such as carbohydrates, cellulose derivatives, gums, lipids, sterols, and proteins.

Familiar examples of emulsions are shaving soap, milk, butter, rubber latex, asphalt, paint, salad dressings, cosmetics, resins, adhesives, detergents, soaps, aerosols, and D.D.T. sprays.

Stable emulsions may sometimes be made by merely shaking or stirring the components together, but usually a more intense agitation is required, and for this purpose some form of colloid mill or homogenizer is used. A colloid mill consists essentially of a high-speed rotor, either plain or grooved, working very close to a stationary surface which forms part of the casing. The clearance may be of the order of 0.001 inch, and must be carefully adjusted and maintained. The premixed liquids and emulsifying agent are forced to pass between the rotor and casing; a thin layer is thus subjected to intense shear, and very fine dispersion results. The Lancaster Disperser is a machine which applies the necessary shear without requiring fine clearances, by means of internal recirculation. The homogenizer comprises a plunger pump which forces the mixed liquids through a spring-loaded valve. The common domestic "cream machine" is of this type.

The general principles of selecting emulsifying agents have been mentioned, but the best agent for stabilizing a particular emulsion is a matter of experiment. In bitumen emulsions for use on roads, bitumens of differing origin may require different emulsifying agents to give the best results. pH control is important, and a buffer salt (such as sodium carbonate or silicate) may be added to the aqueous phase to maintain the required value.

The rate at which emulsions break is sometimes important. Ordinary road emulsions break rapidly on contact with stone, and so cannot be premixed with aggregate, since the bitumen is deposited and forms a tough mass in the mixer. The addition of an alkaline casein solution retards breaking so that the bitumen emulsion can be mixed with stone chips in a mixer and spread on the road. This is the basis of modern "cold asphalt" processes. Undesired emulsions are sometimes encountered in industrial processes, and may be troublesome to separate, such as emulsions of water in crude petroleum, or of lubricating oil in steam condensate. One method of breaking such emulsions is to add an emulsifying agent which tends to produce an emulsion of the opposite type, for example, alkaline sodium oleate produces oil-in-water emulsions, and will therefore tend to break a water-in-oil emulsion. Heating of the emulsion under pressure or the passage of high-tension alternating current through it may also be effective.

*References:* *Introduction to Emulsions*, by G. M. Sutheim (Chemical Publishing Company Inc., Brooklyn); *The Physics and Chemistry of Surfaces*, by N. K. Adams (Oxford University Press); "Surface

Chemistry," A Symposium, 1943 (American Association for the Advancement of Science); *Colloid Chemistry, Theoretical and Applied*, Volumes I-V, by J. Alexander (Reinhold Publishing Corp., New York); *The Theory of Emulsions and Their Technical Application*, by W. Clayton (Blakiston Co., Philadelphia); *Emulsions and Foams*, by Sophia Berkman and Gustav Egloff (Reinhold Publishing Corp., New York).

**ENAMEL PAINTS** — See Paints, Lacquers, and Varnishes.

**ENAMELLED IRON** — Iron plates and ironware are enamelled by coating them (after cleaning) with various silicates containing borates, the mixture as prepared being more readily fusible than glass, and then firing them. The enamels can be coloured by the incorporation of metallic oxides, etc., or rendered opaque with stannic oxide, etc. (See Enamels.)

**ENAMELS** — Ordinary enamels have as their chief constituents, quartz, felspar, clay, soda, and borax, powdered glass and fluorspar being sometimes added, and saltpetre or potash being used as fluxes. Enamels are thus seen to be fusible glasses generally rendered opaque by dissemination throughout the mass of a vitreous substance, such as tin dioxide, infusible at the temperature at which they are made. Up to about 900° C. the tin dioxide exists in a state of suspension in the enamel, but if that temperature be exceeded, real solution takes place and the opacity is diminished. Titanium oxide, zirconium oxide, antimony oxide, sodium metantimonate, and other vitreous substances can be employed in place of the stannic oxide. The opacity is due to differences in refractive index, and is obtained in other cases by the use of arsenious oxide, calcium phosphate, cryolite, etc. Platinum and iridium oxide are sometimes used to produce greys in enamels, and a great variety of other substances (mainly metallic oxides) according to the desired tint and other characteristics, the choice being limited to such materials as will withstand firing.

In making acid-resisting enamels, alkali-earth silicates are mainly used as distinct from the ordinary enamels containing a high percentage of borates, the chief constituents being silica, alumina, lime, and magnesia. Good acid-resisting enamels are only attacked by hydrofluoric, acetic, and formic acids. A temperature as high as 900° C. is sometimes used in their manufacture, and high mechanical strength has to be attained.

One kind of enamel used for glazing cast-iron articles, such as saucepans, consists of powdered flint ground together with calcined borax, fire clay, and a little felspar, made into a paste and applied to the surfaces, which are then dusted over with a glaze mixture composed of felspar, soda-ash, borax, and a small proportion of tin oxide, after which they are dried and fired at a red heat.

Jewellery enamels are prepared from silica, lead oxide, some proportion of sodium peroxide with varying proportions of other oxides for colouring, and in certain cases boric acid.

See *Enamels: Their Manufacture and Applications to Iron and Steelware*, by L. R. Mernagh (C. Griffin and Co., London); Glass, Glazes, and Porcelain. For other classes of enamels see Cellulose, Lacquers, Nitrocellulose, Paints, Pyroxylin, and Varnishes.

**ENARGITE** — A mineral double sulphide of copper and arsenic ( $6\text{CuS}, \text{As}_2\text{S}_2$ ), of crystal system No. 4, and sp. gr. 4.3 to 4.5, found in parts of the U.S.A. and elsewhere.

**ENDOSMOSIS** — See Dialysis, and Osmosis.

**ENDOTHERMIC COMPOUNDS** — See Heat.

**ENERGY** — Energy is an entity postulated to explain the workings of the universe. It is best studied by its interaction upon matter which gives rise to recognizable forms of energy such as kinetic energy, potential energy, electrical energy, magnetic energy, sound energy, light energy, mechanical energy, chemical energy, and heat energy. The different forms of energy are all interchangeable according to well defined laws of physics and thermodynamics. For example, one calorie of heat energy is equivalent to 4.1840 joules of mechanical energy. Einstein's relativity law equates mass and energy with the velocity of light, *i.e.*,  $E=mc^2$ , where  $E$  is the energy,  $m$  is the mass, and  $c$  is the velocity of light. Radiant energy is related to frequency by the equation  $E=h\nu$ , where  $h$  is Planck's constant, and  $\nu$  is the frequency of the radiation. de Broglie's theory correlates "hypothetical waves" and mass particles by  $\lambda=h/mv$ , where  $\lambda$  is the wave length of the particles of mass= $m$  and velocity= $v$ , and  $h$  is Planck's constant.

Energy can best be expressed as the product of two factors—an intensity factor and a capacity or quantity factor—and all forms of energy are generally expressed in either ergs, joules, or calories units. For example:

Energy	=	Intensity factor	×	Capacity factor
Electrical energy (joules)		Potential difference (volts)		Coulombs (ampère-seconds)
Heat energy (calories)		Temperature gradient (degrees)		Heat capacity (calories/degree)
Mechanical energy (ergs)		Force (dynes)		Distance moved (centimetres)

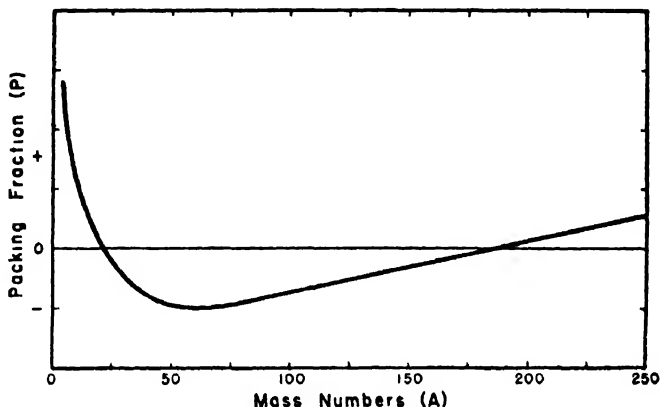
It becomes evident that while no relation exists between volts, degrees, or dynes, nor between ampère-seconds, calories/degree, or centimetres as such, yet mechanical energy is related to electrical and heat energy. All types of energy are interchangeable but not so the individual capacity or intensity factors of which they are composed.

It should be noted that in order to utilize electrical energy there must be a voltage potential gradient moving a quantity of electricity (coulombs), and that mechanical energy is manifested when a force acts through a distance.

Chemical and physical changes are almost invariably accompanied by energy changes and great advances have resulted by studying the laws of thermodynamics relating to these changes.

The chemist is principally interested in the energy of the atoms and molecules due to their kinetic, vibrational, rotational, and internal arrangements of nuclei, electrons, and other structural units. Chemical energy is involved in chemical changes of all types including the nuclear reactions associated with atomic energy. Chemical reactions are commonly brought about by energy supplied in the form of heat, electricity, or light, and when energy is liberated from chemical reactions it appears principally in these forms.

In the organic world in which we find ourselves the sun is the most important source of energy to mankind although cosmic radiation and other sources of energy are being discovered. The chemistry associated with the action of sun energy in the presence of chlorophyll to produce



Mass Defect Curve.

vegetation is of vital importance to our way of life, because from it come our food and fuel. The animal body makes use of the stored chemical energy of food for living, working, and thinking.

Atomic energy is obtained from inside the nucleus of atoms. The basic concepts associated with the release of this type of energy were postulated by Einstein's mass-energy equation previously mentioned. Consider the hypothesis that a nucleus of an atom (see Atoms) consists of protons (whose mass is 1.007582 atomic mass units) and neutrons (whose mass is 1.008930 atomic mass units), the *mass number* ( $A$ ) represents the total number of particles in the nucleus (see Nuclear Chemistry). The *atomic number* ( $Z$ ) is the number of protons in the nucleus, and  $A-Z$  is the number of neutrons in the nucleus. The results of many measurements of the atomic masses of isotopes of elements can be represented most conveniently by considering the deviations of the atomic masses ( $M$ ) from the nearest whole number ( $A$ ), this is called the *mass defect* ( $\Delta m$ ), that is  $\Delta m = M - A$ . Aston defined the term *packing fraction* ( $P$ ) by the relation

$$P = \frac{\Delta m}{A} \times 10^4 = \frac{M - A}{A} \times 10^4.$$

When the packing fraction ( $P$ ) is plotted against the mass number ( $A$ ) the resulting curve has several interesting aspects, namely, packing fractions have small negative values for the elements whose mass numbers lie between 20 and 200; the packing fractions for elements less than 20 and greater than 200 are positive. For most of the lighter elements the packing fractions have relatively large values, except  ${}^4_2\text{He}$  and  ${}^{12}_6\text{C}$ . By definition the packing fraction of  ${}^{16}_8\text{O}$  is zero.

A survey of the data shows that the mass of the nuclei of most elements is less than the sum of the masses of the constituent particles (protons and neutrons). To account for this mass defect use is made of the *Einstein principle of equivalence of mass and energy*,  $E=mc^2$ . If  $\Delta m$  is the mass defect when protons and neutrons combine to form the nucleus of an atom, then the principle says that the change in energy ( $\Delta E$ ) is equivalent to the decrease in mass ( $\Delta m$ ) times the square of the velocity of light ( $c^2$ ) or  $\Delta E=\Delta mc^2$  is the amount of energy released. This energy represents the *binding energy* of the protons and neutrons in the nucleus; if the binding energy is large, the nucleus is stable.

A negative packing fraction means that the mass weight is less than the mass number and consequently mass has been transformed into energy during the formation of that nucleus, and the nucleus should be quite stable. A positive packing fraction would indicate the absorption of energy in the formation of the nucleus and thus a tendency to instability. This last generalization is not strictly correct for elements of small atomic weight because the masses of the proton and neutron are somewhat greater than unity, but for elements of masses greater than 200 the instability shows up in their natural radioactivity. For example, uranium ( $A=238$ ) emits alpha, beta, and gamma rays spontaneously in a well ordered manner and ends up as lead ( $A=206$ ); on the other hand uranium ( $A=235$ ) when bombarded by neutrons will undergo the process of fission where the end products are Kr ( $A=\text{about } 90$ ) and Ba ( $A=\text{about } 140$ ) at the same time releasing large quantities of energy. Krypton and barium both have negative packing fractions and are more stable than the uranium from which they came. The energy released during the fission theoretically is proportional to the differences on the mass defect curve between the uranium and the fission products.

Another corollary from the mass defect curve concerns the front end of the curve between the mass numbers 1 and 20. As is seen in figure (p. 373) the packing fraction difference per unit mass number is much greater than at any other part of the curve. This would indicate that elements of low mass number should condense to form a more stable nucleus of a higher mass number and in so doing emit an amount of energy equivalent to the mass defect between the two elements. For example, to illustrate the relation between mass defect and the meaning of binding energy of a nucleus consider the isotope of lithium of mass number 7 and atomic number 3,  ${}^7_3\text{Li}$ . The lithium nucleus contains 4 neutrons and 3 protons and there are 3 electrons outside the nucleus

to make up the atom. The masses of these particles, including the electrons with the protons, is :

$$4_0n^1 = 4 \times 1.00893 = 4.03572$$

$$3_1H^1 = 3 \times 1.00813 = 3.02439$$

$$\text{Weight of components} = 7.06011 \text{ mass units}$$

$$\text{Weight mass of } {}_3\text{Li}^7 = 7.01816 \text{ mass units}$$

$$\text{Mass defect} = 0.04195 \text{ mass units.}$$

Since one atom mass unit (a.m.u.) =  $1.49 \times 10^{-3}$  ergs, and one electron volt (1 ev.) =  $1.60 \times 10^{-12}$  ergs, and one million electron volts (Mev.) =  $10^6$  ev., then 1 a.m.u. = 931.8 Mev. Therefore 0.04195 a.m.u. (the mass defect for lithium) will be 39.09 Mev. or the binding energy of the  ${}_3\text{Li}^7$  nucleus is 39.09 Mev. This means the lithium nucleus is very stable and any attempt to disrupt it will require the addition of at least this amount of energy. Putting this idea in another way, if lithium were to be formed from neutrons and protons then 39.09 Mev. of energy would be liberated.

Since hydrogen is composed of a proton and an electron and heavy hydrogen (deuterium) consists of one proton, one neutron and one electron it is possible that they could condense to give helium, a more stable nucleus, and have the mass defect liberated as energy. To form one gram mole of helium by condensing an equivalent number of protons (see Atoms)  $8.9 \times 10^{20}$  ergs or  $6.5 \times 10^{11}$  calories of energy will be liberated. This potential energy is available from the hydrogen bomb if a mechanism for starting the condensation can be found. The energy of the sun is in part due to nuclear condensations of this type.

Three fundamental laws are recognized in the thermodynamic study of energy :

(1) **The Law of Conservation of Energy** can be stated in various ways as follows : (a) the total energy of an isolated system must remain constant, although the kinds of energy may be changed from one form to another ; (b) although energy can be converted from one form to another it cannot be created or destroyed ; (c) whenever a quantity of one kind of energy disappears an exactly equivalent amount of another kind or kinds must be produced ; (d) the change in the internal energy  $E$  of the system is equal to the algebraic differences between the heat energy  $q$  and the work energy  $w$  associated with the system, i.e.,  $\Delta E = q - w$  ; (e) the change in heat content  $H$  (enthalpy or total energy) of a system is equal to the algebraic sum of the internal energy  $E$  change and the external work ( $PV$ , pressure times volume change) energy of the system, i.e.,  $\Delta H = \Delta E + \Delta(PV)$ .

(2) **The Second Law of Thermodynamics** is a statistical law stating that : (a) all naturally occurring or spontaneous processes are irreversible ; (b) energy goes from a place of high concentration or potential to a place of low concentration or potential ; (c) water will not of its own self run uphill ; (d) heat will flow naturally from a high temperature to a low temperature ; (e) the maximum work ( $W$ ) that can be obtained from a heat engine is equal to the heat absorbed  $q$

by the engine times a temperature ratio  $\frac{T_2 - T_1}{T_2}$  (where  $T_2$  is the temperature at which heat,  $q_2$ , is taken on and  $T_1$  is the condenser temperature), i.e.,  $W = q_2 \frac{T_2 - T_1}{T_2}$ ; (f) the total amount of entropy

$S$  (heat energy per degree absolute which is unavailable for work energy) in nature is increasing, and the increase in entropy of a system is equal to the heat taken up,  $q$ , in a reversible isothermal system divided by the absolute temperature  $T$  at which it is absorbed, i.e.,

$\Delta S = \frac{q}{T}$ ; (g) the change in free energy  $F$  is equal to the algebraic

difference between the change in heat content  $H$  and the total unavailable heat energy  $T\Delta S$  of the system, i.e.,  $\Delta F = \Delta H - T\Delta S$ .

(3) **The Third Law of Thermodynamics** states that every substance has a finite positive entropy, but at the absolute zero of temperature the entropy may become zero, so that the absolute entropy  $S$  of a perfect crystalline substance at temperature  $T$  is given by integrating  $C_p \frac{dT}{T}$  (where  $C_p$  is the molar heat capacity  $C$  at constant pressure  $P$ ) between the limits of  $T=0$  and  $T=T$ .

*References: Thermodynamics and the Free Energy of Chemical Substances*, by Lewis and Randall (McGraw-Hill Book Co., New York); *Introduction to Atomic Physics*, by Henry Semat (Rinehart and Company, New York); *Outlines of Physical Chemistry*, by F. Daniels (John Wiley and Sons, New York); *Textbook of Physical Chemistry*, by S. Glasstone (D. Van Nostrand Co., New York); *Chemical Thermodynamics*, by F. D. Rossini (John Wiley and Sons, New York). See also Electricity, Heat, Light, Matter, Nuclear Chemistry, and Ultra-Violet Rays.

**ENFLEURAGE** — See Perfumes.

**ENGINEERING (CHEMICAL)** — See Chemical Engineering.

**ENSILAGE** — A process (insufficiently used) for preserving green fodder, such as oats, tares, grass, and maize, for cattle. The pit in which the fodder is stored and pressed down is termed the "silo," and the product is named "silage," the object aimed at being the exclusion of air as far as practicable, thus permitting of a limited anaerobic fermentation, during which much of the protein is transformed into amino-acids, although the mass still contains considerable amounts of cellulose, lignin, and humic substances. The "tower" form of silo is superior to the "clamp" form. Acetic acid is produced during the fermentation, and this acts as a preservative. Lactic acid is also produced when maize and *Sorghum vulgare* are employed. The pigment of silage is stated to be the magnesium-free derivative of chlorophyll, which is soluble in hot alcohol and acetic acid, its production being probably due to the action of carbon dioxide and organic acids developed during the fermentation.

As regards the composition of silage, values have been given as follows: water, 64·7 to 87·5 per cent.; fat, 0·2 to 3·3 per cent.; crude protein, 1·4 to 6·6 per cent.; true protein, 0·86 to 3·71 per cent.; carbohydrate, 6·2 to 17 per cent.; fibre 1·8 to 11·5 per cent.; and ash, 1·7 to 3·5 per cent., as prepared from twenty different materials.

**ENTHALPY** — See Energy.

**ENTROPY** — See Energy.

**ENZYMES** — A class of non-organized, colloidal, nitrogenous substances produced by and associated with certain living animal and vegetable tissues, capable of initiating changes in many chemical substances by way of fermentation, hydrolysis, and oxidation, quite disproportionate to the small amounts employed. They are characterized by the great amount of surface they present, and are in a finer state of division than most other catalytic agents, a state of affairs which naturally promotes their activity, the two phenomena of enzyme and catalytic action being of one class. The action of enzymes is not invariably of a decomposing character, as there is evidence of their ability to serve as synthetic agents in certain cases in appropriate circumstances.

They also exhibit individuality of character, as, for example, in respect of sugars nearly allied, by decomposing some and not others. (See Yeasts.)

Ptyalin, the active ferment of saliva, converts the starch of food into sugar, and the alcoholic fermentation of sugar is due to the enzyme named zymase, as produced by yeast cells. (See Fermentation, and Invertase.) For the most part enzymes seem to act by way of hydrolysis, one such change, for example, being the conversion of cane-sugar or sucrose into glucose and fructose by invertase, brought about by reaction with water;  $C_{12}H_{22}O_{11}$  (Sucrose) +  $H_2O = C_6H_{12}O_6$  (Glucose) +  $C_6H_{12}O_6$  (Fructose). Another such change is the hydrolysis of starch by means of amylopsin or pancreatic diastase into maltose and dextrin; while by a further change, these two saccharoid bodies are converted into ethyl alcohol. Starch is similarly converted by diastase into maltose or malt sugar ( $C_{12}H_{22}O_{11}, H_2O$ ), and malto-dextrins are converted by the enzyme diastase contained in germinated barley. (See Beer.)

Emulsin probably contains several distinct enzymes.

The digestive enzymes comprise many hydrolytic agents capable of replacing the  $-NH_2$  group by the  $-OH$  group, as in the case of urea. Trypsin, one of the pancreatic enzymes, is most active in the presence of alkalis, and decomposes many albuminous bodies down, to the stage of polypeptides, whilst papain (papayotin), which occurs in the papaw-tree (*Carica papaya* L.), is a similar enzyme of vegetable origin. Pepsin, on the other hand, acts only in acid solutions, and while it does not hydrolyse any known polypeptide, it converts albumins into a number of derived compounds, but does not proceed so far in its action as to produce simple amino-acids. It has been shown, however, that pancreatin and trypsin can carry the stage of hydrolysis into

peptone, leucine, tyrosine, aspartic acid, and glutamic acid. (See Amino-acids, and Proteins.)

Hydrolytic enzymes exhibit their maximum activity at about 37° C., and give best results in faintly acid solutions.

The class of enzymes styled *desamidases* are stated to be capable of splitting up the amino-acids into ammonia and hydroxy-acids.

Catalase is a common name for a group of enzymes (one of which can be prepared from germinated beans) which have the power of catalysing hydrogen peroxide, amongst other properties.

By modifying the process of mashing, the amylase in rye and wheat is stated to be sufficient to saccharify the whole starch present in corn (Staiger, *B.C.A.*, B, 1928. 766).

Lipase (one type of which is contained in castor seeds)—an enzyme associated with trypsin—has the power of breaking up fats into glycerol and fatty acids. It is used industrially, and is supposed to be concerned in causing rancidity.

Urease is described as a crystalline enzyme extracted from "Arlco" jack-bean meal by dilute acetone.

There are certain enzymes occurring in all parts of plants and animals named *oxidases* (*oxydases*), or *peroxidases*, which are concerned in acts of oxidation, as distinct from hydrolysis—for example, in the process of respiration.

The *coagulase* class of enzymes can institute changes in various liquids, resulting in the formation of insoluble substances; thus, rennet (chymase) forms curd in milk; thrombose (thrombin) is concerned in the coagulation of blood; and pectase in the production of insoluble pectic acids from the pectin substance of plants.

The particular enzymes associated with bacterial life are necessarily many in number, and must vary in their chemical actions, not merely with the kind of bacteria, but more particularly with the media in which they are allowed to develop, so that their entire range of action is enormous and correspondingly varied in character.

In the action of enzymes as catalysts, the rate is proportional to the strength in which they are present, although the total amount of the change produced by their presence is independent of the amount, given sufficient time. Their activity is wholly destroyed when heated to 100° C., while rennet, thrombose, pepsin, and diastase are inactivated at 45° C. As to the mechanism of enzyme action, it is generally held that adsorption compounds are formed between the enzyme and the substrate, that substance which is decomposed, and that it is these compounds which react with water.

Enzymes are very sensitive to small changes of environment, and there is physiological evidence that their action can be stopped or set free by the living cells, and when separated from these they are more or less unstable; moreover, freedom from associated bodies has a marked effect on their specificity. Their action is often assisted or promoted by associated substances styled co-enzymes or activators, and, on the other hand, it is often interfered with or arrested by other substances, classed as paralyzers or poisons (like sulphur), the latter

behaving, in this sense, as antiseptics do in respect of bacterial processes of decomposition. Possibly there is no such thing as an enzyme, but that which is really dealt with is "a big colloid surface, one part of which contains a certain grouping which, under the proper physical conditions, is able to act as a catalyst," actually participating in the chemical changes that occur, although it is not possible to completely separate the chemically active group from the protective colloid without loss of activity. In this way they may behave in much the same way as the vitamins in respect of their activity.

*References:* R. Willstätter's Faraday lecture on Problems and Methods in Enzyme Research (*J.C.S.*, 1927, 1359); E. F. Armstrong and T. P. Hilditch, respecting the essential parts of a natural enzyme *per se* (*Chem. and Ind.*, **49**, 23 (1930)); "Enzymes in Brewing," by M. A. Pozen (*Ind. Eng. Chem.*, **26**, 1127 (1934)); *Chemistry of Enzyme Actions*, by K. G. Falk (Reinhold Publishing Corp., New York); *Nature of Enzyme Action*, by Sir W. M. Bayliss (Longmans, Green and Co., London and New York); *Enzymes*, by J. B. S. Haldane (Longmans, Green and Co., London and New York); *Enzyme Action and Associated Cell Phenomena*, by F. F. Nord (Baillière, Tindall and Cox, London); *Chemistry and Methods of Enzymes*, by J. B. Sumner and G. F. Somers (Academic Press, New York); *The Enzymes. Chemistry and Mechanism of Action*, by J. B. Sumner and Karl Myrbäck (Academic Press, New York); also Aspergillus, Catalysis, Cytase, Diastase, Emulsin, Maltase, Oxidases, Rennet, Starch, Vitamins and Zymogens.

**EOSIN** ( $C_{20}H_8Br_4O_5$ ) — A red, crystalline dye, soluble in alcohol and acetic acid, prepared by the bromination of fluorescein; it is used for dyeing silk, cotton, and wool; also for making a red ink and vermilion substitute. The potassium salt of tetrabromofluorescein, ( $C_{20}H_6Br_4O_5K_2$ ) is also *commercially* known as *eosin*, and used for the same purposes.

"**EPANUTIN**" — See Phenytoin Sodium.

**EPHEDRA** (**Ma-Huang**) — The dried leaves and stems of various species of *Ephedra*, small plants indigenous to China. It contains about 1 per cent. of total alkaloids, of which about 70 per cent. consists of *l*-ephedrine with *pseudoephedrine* and other closely related alkaloids.

**EPHEDRINE** ( $C_{10}H_{15}ON$ ) — A nearly colourless, crystalline alkaloid, namely,  $\alpha$ -hydroxy- $\beta$ -methylaminopropylbenzene ( $C_6H_5.CH(OH).CH(NH.CH_3).CH_3$ ), extracted from *Ephedra* or obtained by synthesis; soluble in water, alcohol, and ether. A solution in water is dextro-rotatory whilst an alcoholic solution is *lævo*-rotatory. It has an action similar to that of adrenaline in raising the blood pressure and relaxing the smooth muscle of the bronchi and is used in medicine, mainly in the form of its hydrochloride, for the treatment of asthma, hay fever, and other allergic conditions. *Pseudoephedrine*, an isomer of ephedrine, has a less powerful pharmacological action and is less likely to cause unpleasant side-effects.

**EPSOMITE** — See Magnesium (Sulphate).

**EPSOM SALTS** — See Magnesium (Sulphate).

**EQUATIONS** — See Chemical Interactions.

**EQUILIBRIUM** — A balance of forces as experienced in reversible chemical reactions, and illustrated by melting-points at which temperatures, solids and liquids co-exist (in equilibrium). (See Chemical Interactions.)

**EQUILIBRIUM RATIOS** — In the petroleum industry it is the practice to calculate liquid-vapour equilibria using curves of Equilibrium Ratios or “*K*-values,” often incorrectly called Equilibrium Constants (they are far from constant). If  $x$  be the mole fraction of a given component in a liquid mixture, and  $y$  the mole fraction in the vapour in equilibrium with it, then the Equilibrium Ratio for that component under the given conditions is defined by the relation:  $y = Kx$ .  $K$  is a function of temperature and pressure. When the Raoult-Dalton equation holds,  $K = P/\pi$ , where  $P$  = vapour pressure of component at the temperature of the system,  $\pi$  = total pressure of the system. For non-ideal systems  $K = f_x/f_y$ , where  $f_x$  and  $f_y$  are the respective fugacities of the pure liquid component under its own vapour pressure, and of the pure vapour component at the total pressure of the system. C. O. Miller and R. C. Barley (*Ind. Eng. Chem.*, **36**, 1018 (1944)) give curves showing the Equilibrium Ratios of hydrocarbons up to  $C_{14}$  over a wide range of temperatures and pressures. (See Perry's *Chemical Engineers' Handbook* (McGraw-Hill Book Co., New York).)

**EQUIVALENTS** — See Chemical Compounds.

**ERBIUM (Er) and its Compounds** — Atomic weight, 167.2. See Elements for other data. One of the rare-earth group of chemical elements belonging to the yttrium group of the same. Erbium occurs in nature in the minerals *gadolinite*, *yttrantalite*, *euxenite*, etc., together with the earth *yttria*.

The yellow oxide **erbia** ( $Er_2O_3$ ) is obtained by heating the nitrate or precipitated hydroxide; it can be also prepared by heating the oxalate at 575° to 845° C. The salts, including the **chloride** ( $ErCl_3 \cdot 6H_2O$ ), **nitrate** ( $Er(NO_3)_3 \cdot 6H_2O$ ), **bromide** ( $ErBr_3 \cdot 9H_2O$ ), **chlorate** ( $Er(ClO_3)_3 \cdot 8H_2O$ ), **bromate** ( $Er(BrO_3)_3$ ), and **sulphate** ( $Er_2(SO_4)_3 \cdot 8H_2O$ ), etc., are crystalline in character, of a rosy tint, and are soluble in water.

**EREMACAUSIS** — Slow decomposition or consumption by oxidation and other changes as evidenced in nature by the decay of timber, the heating of grain or grass, the decomposition of vegetable matter generally, etc. Low forms of life have much to do with the initiation of the concerned processes, which are retarded by perfect dryness and by a temperature below freezing-point. (See *Ensilage*, and *Wood (Dry-rot)*.)

**ERGOSTEROL** ( $C_{28}H_{48}OH$ ) is obtained from yeast, ergot of rye, and also occurs in human skin, that associated with the latter being converted into one of the D vitamins by the ultraviolet rays of sunlight. Ergosterol has m.p.  $163^{\circ}C.$ ,  $(\alpha)_D -133$ , and absorption maximum  $2,800 \text{ \AA}$ . It is a sterol of the Cholesterol series in its configuration, and has a similar structure to cholesterol, but has two double bonds in ring 2, and a longer side-chain in position 17 (see Sterols). On reduction it yields ergosterol, and on irradiation, as stated above, it yields vitamin D. It has been shown that the product of irradiation is, first lumisterol, then tachysterol, and finally vitamin  $D_2$ .

(See "The Steroids" in H. Gilman's *Organic Chemistry* (John Wiley and Sons, New York); Sterols, Vitamins, and Yeast.)

**ERGOT** — The sclerotium, or resting phase, of the fungus, *Claviceps purpurea*, which arises in the ovary of the common rye plant, *Secale cereale*. It is collected in the U.S.S.R., Austria, Germany, and Spain and contains a number of active principles, including the alkaloids ergotamine, ergotoxine, and ergometrine, together with the amines histamine (misnamed ergotidine and ergamine), and tyramine (misnamed ergamine and uteramine). In addition, ergot contains the inactive alkaloids ergotaminine, ergotinine, and ergometrinine, a sapotoxin, ergotinic acid, acetylcholine, and ergosterol. The active alkaloids have a powerful action in promoting the contractions of the uterus and preparations of ergot are used in obstetrics.

**Ergometrine** (Ergonovine) ( $C_{10}H_{23}O_2N_3$ ), the water-soluble alkaloid of ergot, occurs as a colourless, crystalline substance which becomes coloured on exposure to light and air; slightly soluble in water producing a solution having a blue fluorescence, moderately soluble in dehydrated alcohol and in acetone, sparingly soluble in chloroform and benzene. It exists in two forms, one melting between  $162^{\circ}$  and  $164^{\circ}C.$ , the other at about  $212^{\circ}C.$ ; opt. rot.  $+40^{\circ}$  to  $+43^{\circ}$  (calculated on the anhydrous, solvent-free material, using sodium light). One method of extracting ergometrine is to mix powdered, defatted ergot with aqueous alkali solution or suspension, extract with an organic solvent and evaporate the resulting solution of total alkaloids to dryness under vacuum; the residue is then dissolved in acetone, the water-insoluble alkaloids precipitated by dilution with water and ergometrine recovered by evaporation of the water (U.S. Patent 2192460, March 5, 1940). It is used in medicine in the form of its acid maleate.

**Ergotoxine** ( $C_{35}H_{41}O_6N_5$ ) occurs as a white powder which turns brown on exposure to light and air; almost insoluble in water, soluble in alcohol and acetone. It darkens and decomposes with evolution of gas between  $190^{\circ}$  and  $200^{\circ}C.$  It is used in medicine in the form of its ethanesulphonate, but has been largely replaced by ergometrine, which has a more rapid and less prolonged action than ergotoxine.

**Ergotamine** ( $C_{33}H_{35}O_6N_5$ ) occurs as a colourless crystalline solid which darkens on exposure to light and air; almost insoluble in water, soluble in alcohol and acetone. It is used in medicine either as the tartrate or maleate, its pharmacological action being indistinguishable

from that of ergotoxine. Its main medicinal use is in remedies for migraine.

For a description of the pharmacological properties of the ergot alkaloids see *A Manual of Pharmacology*, by T. Sollmann (W. B. Saunders Co., Philadelphia); and A. C. White, *Quart. J. Pharm.*, **4**, 344 (1943); **1**, 1, (1944); and **2**, 95 (1944).

**"ERIFON"** (Du Pont) — Trade-mark for water solution of antimony and titanium salts. Used to impart flame resistance to cellulose fabrics.

**"ERINOID"** — A condensation product or synthetic resin having a casein base.

**"ERNOLITH"** — A plastic material prepared from waste yeast by treatment with formaldehyde, grinding the product with tar, sulphur, or pigments, and moulding under pressure of 3,000 pounds per square inch at above 90° C.

**ERUCIC ACID** ( $C_{21}H_{41}.COOH$ ) — An unsaturated acid of the olefin series, contained in rape-seed oil, and obtainable from arachidic acid; i.v., 74.3; m.p. 33.5° C. (See Eicosanoic Acid.)

**ERYTHRITE** (Erythrine, Cobalt Bloom) — See Cobalt.

**ERYTHRITOL** ( $C_4H_6(OH)_4$ ) — A tetrahydric alcohol related to *n*-butane as glycerol is to propane. It occurs naturally in lichens, its melting point is 126° C., and the tetranitrate is used in medicine for the same purpose as glycerol trinitrate.

**ERYTHROSIN** ( $C_{20}H_8O_5I_4$ ) — A dye of the composition tetraiodo-fluorescein, whereas the composition of eosin is tetrabromofluorescein.

**ESERINE** — See Calabar Bean, and Physostigmine.

**ESPARTO GRASS** (Halva, Alfa, Alva) — A strong tufty wild grass (*Stipa tenacissima*, very similar to alfalfa), which grows abundantly in Tripoli, Spain, and Algeria, and is largely used in the manufacture of cordage, baskets, sandals, mats, ropes, paper, and by upholsterers as a stuffing material. It contains about 90 per cent. of cellulose. It is boiled with caustic soda or lime water to dissolve the fleshy parts, then bleached. A wax used in soap-making, amounting to 3½ per cent., is obtained as a by-product.

**ESSENCES** — Another name for essential oils; also loosely applied to various aqueous and alcoholic solutions of plant and animal materials, such as lemon, almond, ginger, rennet.

**ESSENTIAL OILS** — Naturally occurring volatile liquids, formed in various plant parts, chiefly the leaves, flowers, or fruits. The main constituents are terpenes which are hydrocarbons having, generally, the empirical formula  $C_{10}H_{16}$ . Other constituents are oxidation products such as alcohols and ketones derived from terpenes.

The essential oils are volatile in steam, have characteristic odours, and leave no oily mark when dropped on to paper. They are inflammable and are almost insoluble in water but soluble in alcohol and ether. Many essential oils are susceptible to oxidation when exposed to air or oxygen, forming oxidized products. Essential oils containing terpenes, in the presence of water, form hydrogen peroxide on oxidation.

Individual constituents of a particular essential oil often bear close structural relationships and groups of substances occurring in two or more oils obtained from related species are also frequently similar in chemical structure.

The part of the plant containing an essential oil varies with different natural orders. In the Umbelliferæ, the essential oil is most abundant in the seeds; in the Aurantiaceæ, both fruits and flowers yield oil; the Rosaceæ contain oil only in the petals; while the Myrtaceæ and the Labiata yield most from the leaves.

The following is a list of the better-known essential oils, showing the nature of their chief constituents:

Camphor oil	Camphor, $C_{10}H_{16}O$ , a ketone together with a terpene
Cinnamon oil	Cinnamic aldehyde, $C_9H_8O$
Citronella oil	Geraniol, $C_{10}H_{18}O$ , an alcohol with citronellal, $C_{10}H_{18}O$ , an aldehyde
Eucalyptus oil	Cineole, $C_{10}H_{18}O$ , an ether, with <i>d</i> -pinene and phellandrene (terpenes)
Lemon oil	Citral, $C_{10}H_{16}O$ , an aldehyde and <i>d</i> -limonene
Orange oil	<i>d</i> -Limonene, a terpene
Peppermint oil	Menthol, $C_{10}H_{20}O$ , an alcohol
Sandalwood oil	Santalol, $C_{15}H_{24}O$ , an alcohol
Spearmint oil	Carvone, $C_{10}H_{14}O$ , a ketone
Turpentine oil (American)	<i>d</i> -Pinene, $C_{10}H_{16}$ , a terpene
Turpentine oil (French)	<i>l</i> -Pinene
Turpentine oil (Russian)	Sylvestrene, $C_{10}H_{16}$ , a terpene
Wintergreen oil	Methyl salicylate, an ester.

Many essential oils are used in perfumery, in medicine for their carminative and flavouring properties, and in confectionery. (See *Cyclopædia of Perfumery*, E. J. Parry (J. and A. Churchill, London); *The Essential Oils*, H. Finckmore (Ernest Benn, Ltd., London); Schimmel and Co.'s reports; Balsams, Perfumes, and Terpenes.)

**ESTER GUM** — See Gums and Resins.

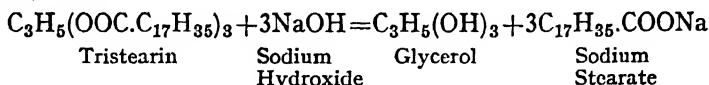
**ESTER NUMBER** — See Fats.

**ESTERS AND ESTERIFICATION** — Many alcohols react with mineral and organic acids to form what are termed alkyl (ethereal) salts or *esters*; for example, ethyl alcohol and acetic acid by interaction give ethyl acetate and water ( $C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O$ ), and the process is known as esterification.

**Ethyl Valerate** ( $C_4H_9COOC_2H_5$ ) is a colourless liquid of pleasant odour, of sp. gr. 0.877 and b.p.  $145^\circ C.$ ; soluble in water, alcohol, and ether, and used in compounding perfumes, etc.

Monobasic acids such as nitric acid yield only one kind of ester, termed "normal or neutral esters," but dibasic acids yield two series, termed "acid esters" and "neutral esters"; thus ethyl nitrate is  $(C_2H_5)NO_3$ , while there are the two ethyl sulphates  $(C_2H_5)HSO_4$  and  $(C_2H_5)_2SO_4$ . The acid esters as a class are odourless, readily soluble in water, much less stable than the neutral series, and cannot be volatilized without decomposition.

The fats, palmitin, stearin, and olein are solid esters, or glyceryl esters (glycerides) of respectively palmitic, stearic, and oleic acids, and are resolved by hydrolysis into glycerol (glycerine) and the several fatty acids; thus



The monoglycerides and the diglycerides are, it is believed, absent from natural freshly prepared fats and oils. (See Fats, Glycerides, and Soaps.)

Many of the esters form part of the odorous constituents of essential oils, and some of the better-known commercial ones listed below are individually described in the context:

Amyl acetate	Benzyl benzoate	Geranyl acetate
Amyl benzoate	Benzyl chloride	Glyceryl triacetate
Amyl borate	Butyl acetate	Methyl acetate
Amyl butyrate	Butyl formate	Methyl benzoate
Amyl formate	Dimethyl sulphate	Methyl salicylate
Amyl salicylate	Ethyl acetoacetate	Tricresyl phosphate
Amyl valerate	Ethyl salicylate	Triphenyl phosphate
Benzyl acetate		

The amyl esters of formic, acetic, and hexoic (caproic) acids are among the odorous constituents of apples, and many esters are used in perfumery and for flavouring fruit essences, etc.

**ESTRADIOL** — A female sex hormone dihydrotheelin. (See Theelin.)

**ESTROGENS** — Hormone substances which cause the development of female sex characteristics. (See Androgens, Estradiol, and Theelin.)

**Et** — A symbol used for ethyl ( $C_2H_5$ ) radical.

**"ETELINE"** — See Solvents.

**"ETHAMOLIN"** — See Ethanolamine Oleate.

**ETHANAL** — See Aldehydes (Acetaldehyde).

**ETHANE** — See Hydrocarbons.

**ETHANOL** — Ethyl alcohol. (See Alcohols.)

**ETHANOLAMINES** — See Triethanolamine.

**ETHANOLAMINE OLEATE INJECTION** ("Ethamolin," "Neo-Vari-cane") — A sterile solution containing 5 per cent. of ethanolamine oleate and 2 volume per cent. of benzyl alcohol. Used in medicine as a sclerosing agent for the treatment of varicose veins.

**ETHENE (Ethylene, Olefiant Gas)** — See Ethylene, and Hydrocarbons.

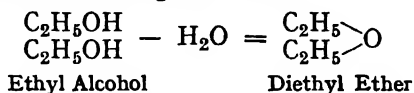
**ETHENOL** — See Vinyl Alcohol.

**ETHER (Nitrous)** — See Nitrous Ether.

**ETHER (Sulphuric)** — Diethyl ether. (See Ethers.)

**ETHEREAL SALTS** — See Esters.

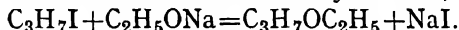
**ETHERS** — Into the category of ethers fall all those compounds which contain the group  $R-O-R$ , where  $R$  represents two similar or dissimilar alkyl or aryl groups. They may be regarded as the anhydrides of alcohols or oxides of the organic radicals.



The actual formation by the abstraction of the elements of water from an alcohol is not a practical proposition except in the case of the most important ether, diethyl ether; most of the others are prepared by one of the following general methods:

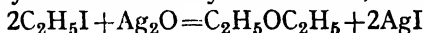
(1) By heating the alcohol with sulphuric acid, phosphoric acid, or benzenesulphonic acid, *e.g.*, the case of diethyl ether above; this method can be used only on primary alcohols, as secondary or tertiary alcohols give olefines by this treatment.

(2) By the action of sodium alkoxides on alkyl halides, *e.g.*,



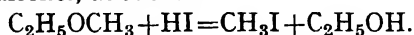
(3) By the alkylation of alcohols or phenols by means of dialkyl sulphate, *e.g.*,  $\text{C}_6\text{H}_5\text{OH} + (\text{CH}_3)_2\text{SO}_4 = \text{C}_6\text{H}_5\text{OCH}_3 + \text{CH}_3\text{HSO}_4$ . This reaction is carried out in the presence of sodium hydroxide.

(4) From alkyl halides and dry silver oxide, or mercuric oxide, *e.g.*,



Those ethers in which both alkyl radicals are the same are called simple ethers, while those in which the alkyl groups are different are known as compound, or mixed ethers.

Ethers are very stable chemically, being usually unaffected by the common alkalis, metallic sodium, or ammonia. They are attacked by strong mineral acids, which split them, for example, into an alkyl halide and an alcohol, as follows:



In the case of hydriodic acid the method can be made quantitative, and as the smaller radical always associates itself with the iodine atom to yield methyl iodide (in the case indicated), a method of estimating methyl ethers is available, the methyl iodide being distilled away and estimated. The method is known as Zeisel's determination of methoxyl.

**Ethyl Ether (Diethyl Ether)**, also commonly known by the names

of "sulphuric ether" and "vitriol ether," is a mobile liquid of characteristic odour, soluble in alcohol, slightly soluble in water, very volatile and inflammable. It is prepared by distillation following upon the action of sulphuric acid on ethyl alcohol, and can also be made by passing alcohol vapour at  $250^{\circ}\text{C.}$  over specially prepared aluminium oxide. It absorbs oxygen from the air, yielding hydrogen peroxide with acidified water. On account of its highly inflammable nature, high vapour pressure at room temperatures, and the formation of peroxide, ether is one of the most hazardous of common chemicals. It boils at  $34.5^{\circ}\text{C.}$ , has a sp. gr. of 0.714, and is an excellent solvent of oils, fats, and many organic substances. Apart from its extensive use as an anæsthetic, it is used commercially in the colour industry and in the preparation of collodion, smokeless gunpowder, etc. It has been found by Baker that the vapour density of ether dried for ten years is 81.7—that is, more than double the normal one. When a mixture of ether vapour and air is allowed to expand suddenly into an evacuated tube it ignites.

**Methyl Ether**  $(\text{CH}_3)_2\text{O}$  is gaseous at ordinary temperatures, but liquefies at  $-24.9^{\circ}\text{C.}$ , and is prepared on a considerable scale for use in refrigerators, owing to the intense coldness developed on its evaporation.

**Vinyl Ether**  $(\text{CH}_2 : \text{CH}-\text{O}-\text{CH} : \text{CH}_2)$  is prepared by the action of potassium hydroxide on  $\beta$ ,  $\beta'$ -dichloro-diethyl ether. It boils at  $31^{\circ}\text{C.}$ , and is soluble in about 100 parts of water. It is used as a general anæsthetic. The main drawback to its use is its unstable nature, and the toxicity of its oxidation products.

See Monobutyl, Monoethyl, and Monomethyl Ethers of Diethylene and of Ethylene Glycol.

**ETHIDES**—Combinations of metals with the radical ethyl, such as zinc ethide or diethyl zinc  $(\text{Zn}(\text{C}_2\text{H}_5)_2)$ .

**ETHISTERONE** (Anhydrohydroxyprogesterone, Ethinyltestosterone, Pregnenolone)  $(\text{C}_{21}\text{H}_{28}\text{O}_2)$ —A white, odourless, and tasteless crystalline powder, namely, 17-ethinyl- $\Delta^4$ -androstene-17-ol-3-one; soluble in hot acetone; sparingly soluble in chloroform; insoluble in water; m.p.  $269^{\circ}$  to  $275^{\circ}\text{C.}$  It is prepared by the addition of acetylene to the ketonic group in position 17 in dehydroisoandrosterone, which is obtained by the oxidative degradation of sterols such as cholesterol. A method for its preparation by reacting potassium acetylide with dehydroisoandrosterone in anhydrous ammonia is described in F.I.A.T., Final Report No. 996; and the synthesis of ethisterone by Schwenk in *The Chemistry and Physiology of Hormones* (Amer. Ass. Adv. Sci., 1944). Ethisterone has the physiological action of the hormone of the corpus luteum, progesterone, but is active when given by mouth.

**"ETHOCEL"**—Trade name for ethyl cellulose.

**ETHYL**—The radical  $\text{CH}_3\text{CH}_2$ , or  $\text{C}_2\text{H}_5$ , as contained in ethyl alcohol  $(\text{C}_2\text{H}_5\text{OH})$ . The preparation of free ethyl and some of its properties are described by Paneth and Lautsch. (See Radicals.) The trade name "Ethyl" applies to tetraethyl lead as manufactured and used as an anti-knock material for motor fuel.

**ETHYL ACETATE** — See Esters.

**ETHYL ALCOHOL** — See Alcohols.

**ETHYL ALDEHYDE** — See Aldehydes.

**ETHYL BENZOATE** — See Esters.

**ETHYL BROMIDE (Monobromoethane)** ( $C_2H_5Br$ ) — A liquid substitution product of ethane, of sp. gr. 1.430 and b.p.  $38.0^\circ C.$ , miscible with alcohol and ether; formerly used as an anæsthetic. With magnesium metal it reacts (Grignard compound), and this is used with lead chloride to make tetraethyl lead.

**ETHYL BUTYRATE** — See Esters.

**ETHYL CAPRYLATE** — See Esters.

**ETHYL CARBONATE** ( $(C_2H_5O)_2CO$ ) — A liquid of pleasant odour, sp. gr. 0.979 and b.p.  $126^\circ C.$ , soluble in alcohol, but not in water; used as a solvent, and produced by the interaction of carbonyl chloride and excess ethanol.

**ETHYL CELLULOSE** — A white, granular ether, of 47–48 per cent. ethoxy content, of m.p.  $140^\circ C.$ , non-inflammable, stable to light, resistant to acid and alkalis, miscible with nitrocellulose, and, when more than 50 per cent. of ethyl cellulose is used, the burning rate of the product is decreased and the flexibility increased, miscible also with linseed, soy bean, and perilla oils. It is used in films, lacquers, and plastics. (See "Properties and Uses of Ethylcellulose," by W. Koch (*Ind. Eng. Chem.*, 29, 687 (1937)); and "Ethocel.")

**ETHYL CHLORIDE (Monochloroethane)** ( $C_2H_5Cl$ ) is at ordinary temperature a gas which is easily condensed to a colourless liquid state. It boils at  $12.2^\circ C.$ , and is soluble in alcohol and ether. It is produced by passing dry hydrochloric acid gas into ethyl alcohol in presence of zinc chloride, and manufactured by mixing strong sulphuric acid with alcohol, and after standing some time, followed by dilution with water and addition of some potassium chloride, distilling the mixture.

A series of chlorine substitution products may be obtained from it, isomeric with those obtainable from ethylene dichloride, the final product  $C_2Cl_6$  being identical, but those derived from ethyl chloride are not so readily decomposed by alcoholic potash and boil at different temperatures from the other series. Mixed with a small quantity of chloroform, it is used as an anæsthetic, and exercises a prolonged effect. Ethyl chloride constitutes a very convenient material for refrigeration, particularly when rendered non-inflammable by means of methyl bromide. It does not attack metals.

**ETHYL CINNAMATE** — See Esters.

**ETHYL ETHER** — See Ethers.

**ETHYL FORMATE** — See Esters.

**"ETHYL GASOLINE"** — Anti-knock motor fuel. (See Motor Spirit.)

**ETHYL MORPHINE** — See Dionin.

**ETHYL NITRATE** — See Esters.

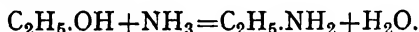
**ETHYL NITRITE** — See Nitrous Ether.

**ETHYL PETROL ("ESSO")** — A proprietary brand of anti-knock motor spirit stated to contain tetraethyl lead and ethylene dibromide.

**ETHYL SILICATE**  $((C_2H_5O)_4Si)$  — A colourless liquid, of sp. gr. 0.933 and b.p.  $165^\circ C.$ , has a faint odour. Used as a preservative and hardener for stone and concrete, and as a weather- and acid-proof cement, owing to the fact that it hydrolyses to form silicic acid, which is then spontaneously dehydrated to an adhesive form of silica.

**ETHYL VALERATE** — See Esters.

**ETHYLAMINE**  $(C_2H_5.NH_2)$  — In the anhydrous state this compound is a colourless, mobile, inflammable liquid of sp. gr. 0.689 at  $15^\circ C.$  and b.p.  $16.6^\circ C.$  It burns with a yellow flame, is soluble in water, but may be expelled from the solution by boiling. It can be prepared in a number of ways, including the decomposition of ethyl cyanate with potassium hydroxide, the action of ammonia upon ethyl bromide, and the catalytic (exothermic) action of a silica or alumina gel upon ethyl alcohol and ammonia :



Like other amines of its class, it has an alkaline reaction, ammoniacal odour, and combines with hydrochloric acid, etc., to form salts. (See Amines.)

**ETHYLATION** — Introduction of the ethyl group into compounds. In various instances the following reagents are used, namely, ethyl alcohol, ethyl chloride, ethyl iodide, diethyl sulphate, and sodium ethoxide. (See *Organic Reactions*, by Roger Adams (John Wiley and Sons, New York).)

**ETHYLENE (OLEFIANT GAS)**  $(C_2H_4)$  — A gas, being the simplest compound containing the ethylenic linkage or double bond between two carbon atoms, of graphical formula  $\begin{matrix} HCH, \\ H\dot{C}H \end{matrix}$  sp. gr. 0.97 (Air=1.00), m.p.  $-169^\circ C.$ , b.p.  $-104^\circ C.$ , liquid at  $10^\circ C.$ , and 50 atm. pressure. The gas is colourless, of slight odour, acts as an anæsthetic when inhaled, is insoluble in water, burns when ignited in air with a luminous flame, and its presence in coal gas is chiefly responsible for the luminosity of the latter, forms an explosive mixture with air, and is of high fuel value (1615 B.Th.U. per cu. ft.).

Ethylene is used in the preparation of its derivatives (see accompanying chart), as an anæsthetic, as a fuel with oxygen for high temperature flame, and as a colouring and ripening agent for various fruits.

See Alcohol (Ethyl), Fruits, and Hydrocarbons (Olefines).

**ETHYLENE DIAMINE** ( $\text{C}_2\text{H}_4(\text{NH}_2)_2$ ) — A colourless liquid, b.p.  $117^\circ \text{C}$ . and sp. gr. 0.892, made from a mixture of ethylene chloride and ammonia, followed by distillation; used as a solvent of albumin, fibrin, casein, and sulphur compounds, as an emulsifying agent, and in the

preparation of pharmaceuticals, dyes, and rubber accelerators. It forms co-ordination compounds with many metals, these being examples of chelate compounds.

**ETHYLENE DICHLORIDE** (Ethylene Chloride, Dutch Liquid, Ethylene Glycol Dichloride, 1,2-Dichloroethane) ( $\text{CH}_2\text{Cl}.\text{CH}_2\text{Cl}$ ) is prepared by the direct combination of ethylene and chlorine at  $0^\circ\text{C}$ ., with subsequent distillation. It is a heavy, oily, colourless liquid, insoluble in water, soluble in alcohol and ether, and of pleasant odour (somewhat like chloroform). It is now made in considerable quantities in the U.S.A. from petroleum gases containing a high percentage of ethylene. It crystallizes at a low temperature, boils at  $83.7^\circ\text{C}$ ., has a density of 1.257 at  $0^\circ\text{C}$ ., finds some use as an anæsthetic, and constitutes a valuable solvent of oils, fats, waxes, certain resins, and gums. (See Solvents.) It is isomeric with ethylidene chloride ( $\text{CH}_3.\text{CHCl}_2$ ).

By the continued action of chlorine, it yields a series of other substitution products—viz.,  $\text{C}_2\text{H}_3\text{Cl}_3$ ,  $\text{C}_2\text{H}_2\text{Cl}_4$ ,  $\text{C}_2\text{HCl}_5$ , and  $\text{C}_2\text{Cl}_6$ , the final member being identical with the substance of same formula obtainable from ethyl chloride.

When these various ethylene chlorides are subjected to the action of alcoholic potash they are decomposed, and yield the so-called chlor-ethylenes as follows :

$\text{C}_2\text{H}_4\text{Cl}_2$  gives chlorethylene,  $\text{C}_2\text{H}_3\text{Cl}$ , by loss of  $\text{HCl}$ .

$\text{C}_2\text{H}_3\text{Cl}_3$  gives dichlorethylene,  $\text{C}_2\text{H}_2\text{Cl}_2$ , by loss of  $\text{HCl}$ .

$\text{C}_2\text{H}_2\text{Cl}_4$  gives trichlorethylene,  $\text{C}_2\text{HCl}_3$ , by loss of  $\text{HCl}$ .

$\text{C}_2\text{HCl}_5$  gives per(tetra)chlorethylene,  $\text{C}_2\text{Cl}_4$ , by loss of  $\text{HCl}$ .

(See Ethyl Chloride, and Solvents.)

**ETHYLENE GLYCOL** (Glycol, 1,2-Dihydroxyethane) ( $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$ ) — A clear, sweet, syrupy liquid of sp. gr. 1.115 and b.p.  $197.5^\circ\text{C}$ . soluble in water, alcohol, and ether. It is made in large quantities from the ethylene of natural gas and that produced by cracking petroleum hydrocarbon oils; ethylene chlorohydrin being first obtained by use of hypochlorous acid, and then converted into the glycol. It can also be prepared from ethylene iodide by silver acetate and saponification. A 35 per cent. solution in water freezes at about  $-20^\circ$ , and a 45 per cent. by volume solution is recommended as an "anti-freeze" material for motor-car radiators, meeting severe conditions. It is used for making nitroglycol and ethanalamines; is a valuable lubricant for wool-spinning (dispensing as it does with the costly scouring for oil elimination after spinning); serves as a solvent for certain dyes and other substances; and is superior to glycerol for some purposes, including its use as an anti-freeze agent. (See "Industrial Applications of the Glycols," by H. B. McClure (*Ind. Eng. Chem., News Ed.*, 17, 149 (1939)).)

**ETHYLENE OXIDE**  $\left( \text{O} \begin{array}{c} \diagup \text{CH}_2 \\ | \\ \diagdown \text{CH}_2 \end{array} \right)$  — A colourless gas, of b.p.  $13.5^\circ\text{C}$ ., and m.p.  $-111^\circ\text{C}$ ., made from ethylene chlorohydrin by boiling with

sodium hydroxide solution. It is used as a fumigant, and in synthetic chemistry to lengthen carbon chains by two C-atoms. When Grignard reagent is used the resulting product is a primary alcohol. (See Ethylene (Chart), and Fumigation.)

**ETHYLIDENE CHLORIDE** — See 1,1-Dichloroethane.

**ETHYLMORPHINE** — See Dionin.

**ETHYNE** — See Acetylene.

**EUCAINE** — See Benzamine Hydrochloride, and Benzamine Lactate.

**EUCALYPTOL (Cineol)** — See Cineol, and Essential Oils.

**EUCALYPTUS OILS** — Essential oils obtained by rectifying the oil distilled from the leaves of various species of *Eucalyptus*, of which there are upwards of 300 ranging from very large trees to dwarf bushes growing in Australia. The oils vary considerably in their constituents, which include cineole, phellandrene, citral (geranial), and terpenes. The oil used in medicine is obtained from *Eucalyptus polybractea*, *E. dumosa* and other species yielding oils containing a high proportion of cineole but little phellandrene; sp. gr. 0.910 to 0.930; opt. rot.  $-5^{\circ}$  to  $+5^{\circ}$  at  $20^{\circ}\text{C}$ .; ref. ind. 1.458 to 1.470 at  $20^{\circ}\text{C}$ .; soluble in alcohol, ether and chloroform.

Apart from their medicinal use, eucalyptus oils are used in the flotation process of ore concentration. Their calorific value is high and they can be mixed with petrol and benzene, acting as decarbonizing agents and thus keeping cylinders and pistons of internal combustion engines free, to some extent, from carbon.

**Eucalyptus globulus** yields an oil having a high cineole content and for this reason it was formerly extensively cultivated in Australia. It has now been replaced by higher yielding varieties and the unmixed oil of *E. globulus* is no longer available in commerce. It contains from 50 to 80 per cent. of cineole together with some pinene, phellandrene, and cymene.

**Eucalyptus amygdalina** yields an oil, the chief constituent of which is phellandrene; it is not so pungent in odour as the globulus oil; sp. gr. 0.855 to 0.890 at  $15^{\circ}\text{C}$ .; ref. ind. 1.474 to 1.480 at  $20^{\circ}\text{C}$ .; opt. rot.  $-25^{\circ}$  to  $-80^{\circ}$  at  $20^{\circ}\text{C}$ .

The oil from **Eucalyptus phellandra** has a sp. gr. of 0.895 to 0.912 at  $15^{\circ}\text{C}$ . and contains from 20 to 30 per cent. of cineole with phellandrene, pinene, terpineol, and geraniol.

**Eucalyptus maculata** (var. *citriodora*) yields "Lemon-scented" Eucalyptus oil which contains from 90 to 95 per cent. of citronellal; sp. gr. 0.870 to 0.905 at  $15^{\circ}\text{C}$ .; ref. ind. 1.455 to 1.460 at  $20^{\circ}\text{C}$ .; opt. rot.  $-1^{\circ}$  to  $+2^{\circ}$  at  $20^{\circ}\text{C}$ .

**Eucalyptus dives** produces an oil which contains a large proportion of piperitone and is used in the manufacture of thymol. It also contains phellandrene, pinene, and cineole; sp. gr. 0.871 to 0.902 at  $15^{\circ}\text{C}$ .; opt. rot.  $-55^{\circ}$  to  $-64^{\circ}$  at  $20^{\circ}\text{C}$ .; ref. ind. 1.480 to 1.481 at  $20^{\circ}\text{C}$ . (See Thymol.)

**Eucalyptus piperita** also yields an oil containing piperitone (about 44 per cent.) and phellandrene. (See Menthol, and Piperitone.)

For an account of the seasonal variation in oil obtained from *E. cneorifolia*, see P. A. Berry, *J. Proc. Austral. Chem. Inst.*, **14**, 173, 383 (1947). Further information on eucalyptus oils is given in *The Essential Oils*, J. H. Finnmere (Ernest Benn, London).

**"EUCERIN"** — A proprietary preparation consisting of a mixture of paraffins and steroid alcohols obtained from lanolin. It is capable of absorbing an equal weight of water to form a water-in-oil emulsion and is used as an ointment base.

**EUCLASE (Prismatic Emerald)** — A native silicate of aluminium and beryllium ( $2\text{BeO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2, \text{H}_2\text{O}$ ); crystal system No. 5; sp. gr. 3.1.

**EUDIOMETER** — A simple form of this apparatus, as used for the examination of gases, is a long glass tube, closed at the one end and open at the other, graduated into cubic centimetres. At the closed end, thin wires of platinum are fused through the glass, and thence pass outside, so that they can be connected with the wires of an electric coil. In using it to demonstrate the composition of water, a mixture of 2 volumes of hydrogen and 1 volume of oxygen is introduced into the tube, which is then inverted and placed with its open end in a trough of mercury. Upon causing an electric spark to pass from end to end of the wires, the gases combine with explosive force. In this way, it is found that these respective quantities combine to form water. (See Voltmeter.)

Using a mercury bath, this form of eudiometer may be used also to demonstrate the proportion of oxygen present in a given volume of air by inverting the graduated tube containing some air (the rest of the tube being occupied by mercury) over the bath, and introducing, by means of a pipette having a recurved end, some few cubic centimetres of a mixture of 1 part of pyrogallic acid in 6 parts of water rendered alkaline with caustic potash. This solution rises up through the mercury in the tube, absorbs the oxygen, becomes dark brown in colour in consequence, and leaves the nitrogen unabsorbed, the diminution in volume thus becoming apparent. (See Organic Analyses.)

**EUFLAVINE** ( $\text{C}_{14}\text{H}_{14}\text{N}_3\text{Cl}$ ) — An orange-red, acridine dye, namely, 3,6-diamino-10-methylacridinium chloride, prepared from acriflavine by precipitation with sodium chloride; slightly soluble in water and alcohol. It is used in medicine as an antiseptic. (See Acriflavine.)

**EUGENOL** ( $\text{C}_{10}\text{H}_{12}\text{O}_2$ ) — A colourless or pale yellow liquid, namely, 2-methoxy-4-allylphenol, obtained by extraction from clove oil with sodium hydroxide and subsequent decomposition of the sodium eugenate with dilute sulphuric acid. It has a sp. gr. of 1.072 to 1.074 and boils at about  $253^\circ \text{C}$ .; soluble in alcohol and ether, slightly soluble in water. It is used in dentistry as an antiseptic and local analgesic, and in industry as a constituent of cellulose acetate varnishes. Eugenol also occurs (about 79 per cent.) with safrole (about 14 per cent.) in the oil obtained by steam distillation of Massoi bark (obtained from a species of *Cinnamomum*) widely distributed in New Guinea.

Isoeugenol is made from eugenol on a large scale in the manufacture of vanillin. To effect this, the eugenol or oil of cloves is heated with strong caustic potash whereby any terpenes present are distilled off, and then the potassium salt of eugenol is dissolved in aniline and, after removal of the excess of potassium hydroxide, is heated to 185° C. The resulting potassium compound of isoeugenol is then mixed with nitrobenzene and caustic potash and the nitrobenzene and aniline subsequently distilled off by use of steam. The product is next acidified and the isoeugenol extracted with toluene from which it is freed by distillation and subsequently purified by recrystallization from toluene and finally from water. It has a boiling point of about 267° C. and is said to have about 50 times the flavouring power of natural vanilla bean. (See also Cloves, and Vanilla.)

**"EULAN"** — Trade-mark of a series of sulphonic, carboxylic acid, and sulphonyl chloride derivatives of aromatic hydrocarbons, applicable for moth-proofing of wool. These are stated to be odourless, colourless, harmless to human skin and fabrics, and affording permanent protection against moth in articles of clothing. An aqueous solution is used when articles have to be immersed, or one of solution in naphtha for dry cleaning.

**"EULISSIN"** — A proprietary name for a solution of decamethonium iodide (see same) containing 5 mg. in 2.5 ml., used as a muscle relaxant for surgical anaesthesia.

**EUONYMUS** — The dried root-bark of the American spindle-tree, *Euonymus atropurpureus*. It contains an alcohol-soluble, oleo-resinous extract, known as euonymin, which possesses mildly laxative and tonic properties.

**EUPHORBIUM** — See Gums and Resins.

**EUPHORIN (Phenylurethane)** — Prepared from ethyl chloroformate and aniline, possessing analgesic character.

**EUROPIUM (Eu)** — Atomic weight, 152.0. See Elements for other data ; also oxides. One of the rare-earth group of chemical elements, and belonging to the scandium group of the same. Europium occurs in the minerals *samariskite*, *orthite*, *cerite*, and *gadolinite*.

**EUSOL** — An antiseptic solution containing hypochlorous acid ; prepared by interaction between so-called chloride of lime and boric acid in aqueous solution. (See Dakin's Solution, and "Milton").

**EUTECTIC** — The melting point of pure lead is 327° C., but when tin is added to lead the melting point of the mixture decreases as the percentage of tin increases until a mixture of 63 per cent. by weight tin and 37 per cent. by weight lead is reached which has a melting point of 180° C. The melting point of pure tin is 232° C. and when lead is added the melting point of the mixture decreases until a composition of 63 per cent. by weight tin and 37 per cent. by weight lead is obtained which as above has a melting point of 180° C. Thus 180° C. is the lowest temperature that a mixture of tin and lead can have and remain liquid, and the mixture is 63 per cent. tin and 37 per cent. lead. This

mixture of 63 per cent. tin and 37 per cent. lead is called the *eutectic mixture* and  $180^{\circ}\text{C}$ . is called the *eutectic temperature*. The diagram shows how the various phases of tin and lead mixtures are related to temperature and composition. The area above the lines AB, BC is entirely in the liquid phase at all temperatures and concentrations shown. The area bounded by lines AB, BD represents two phases containing pure solid lead and liquid mixture of composition given by points on the line AB. The area bounded by lines BC, BE represents solid tin with liquid mixture of composition given by points on the line BC. All the area below the line BDE represents solid phase mixture made up of varying percentages of tin and lead. That part of the solid which solidified in the ratio of 63 per cent. tin and 37 per cent. lead is called a *eutectic mixture* because it crystallizes in a peculiar manner with interlocking microscopic plates.

Many mixtures have eutectic mixtures and temperatures, the following are a few examples :

Component 1		Component 2		Eutectic Temperature
Name	Melting Point	Name	Melting Point	
Antimony ..	$630^{\circ}\text{C}$ .	Lead ..	$327^{\circ}\text{C}$ .	$246^{\circ}\text{C}$ .
Bismuth ..	$317^{\circ}\text{C}$ .	Cadmium ..	$268^{\circ}\text{C}$ .	$146^{\circ}\text{C}$ .
Aluminium ..	$657^{\circ}\text{C}$ .	Silicon ..	$1,412^{\circ}\text{C}$ .	$578^{\circ}\text{C}$ .
d-Pinene ..	$-64^{\circ}\text{C}$ .	l-Pinene ..	$-64^{\circ}\text{C}$ .	$-120^{\circ}\text{C}$ .

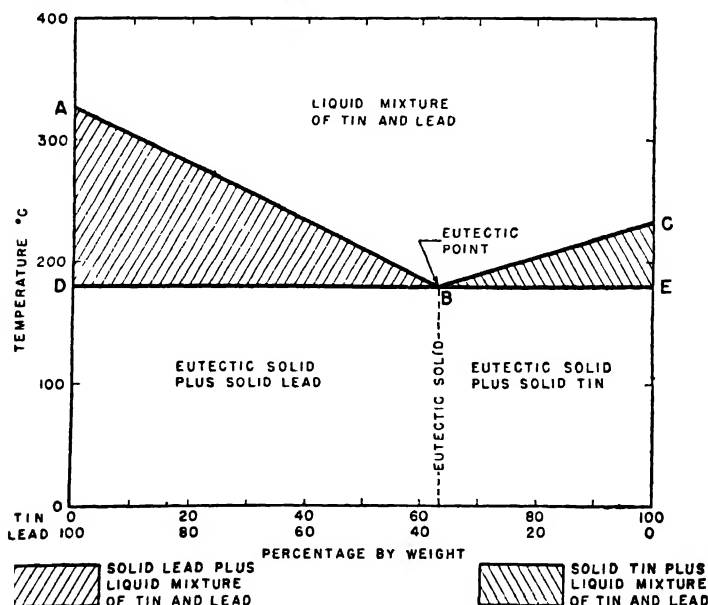


Diagram Showing the Melting Point Curve for Tin and Lead

*References:* *Textbook of Physical Chemistry*, by Glasstone (D. Van Nostrand Co., New York); *Treatise on Physical Chemistry*, by Taylor (D. Van Nostrand Co., New York); *The Phase Rule and its Applications*, by Findlay and Campbell (Longmans, Green and Co., New York and London); *Aqueous Solutions and Phase Diagrams*, by Purdon and Slater (Edward Arnold and Co., London); "An Introduction to the Phase Rule," by Deming (*J. Chem. Educ.*, **16**, 215, 260 (1939)). (See Alloys, Dystectic Mixture, Iron-Carbon system under Iron, and Solution.)

**EUTECTOID** — Composition of a solid solution which decomposes completely by an isothermal reaction, and is further characterized by the point where solid solubility curves meet at a minimum temperature value. (See the Pearlite point in the Iron-Carbon system under Iron.)

**EUXAMITE** — A radioactive radium earth found in Brazil.

**EUXENITE** — A complex mineral containing erbium, titanium, cerium, etc.

**EVAPORATION** — Literally synonymous with Vaporization, but in chemical practice the term "Evaporation" is usually reserved for operations in which a dissolved substance is concentrated or obtained as a solid residue by vaporization of the solvent. Evaporation plays an important part in many industrial processes, such as salt and sugar manufacture, and sulphuric acid concentration.

The most primitive kind of evaporator is a shallow basin exposed to the sun's rays, such as is still used in hot countries for obtaining salt. The simplest evaporator using artificial heat is an open pan, either fired directly or provided with a steam jacket. The open pan is little more than an enlarged version of the laboratory evaporating dish or the kitchen saucepan; it is even less efficient than these vessels for the reason that, owing to its greater size, it has less heating surface per unit volume of liquid.

Modern evaporator design aims at extended heating surfaces, high heat transfer coefficients, and the maximum degree of heat economy. The heating medium is nearly always steam. Extended heating surfaces are secured by tubular construction, high heat transfer coefficients by rapid circulation of liquid, and maximum heat economy by the use of the multiple effect principle. A multiple effect evaporator consists of a series of closed vessels maintained at successively lower pressures, so that the liquid in them boils at successively lower temperatures. The first stage is heated by process steam, and the vapour evolved from the solution being concentrated is caused to condense on the heating surfaces of the second stage, thereby boiling the liquid contained in it. Vapour from the second stage in turn boils the liquid in the third stage, and so on. The solution to be concentrated enters at the final stage in which the highest vacuum is maintained, and is passed through successive stages to the first, which may be at or above atmospheric pressure. Reduced pressures in the various stages are maintained by vacuum pumps or steam-jet ejectors. In an evaporator with  $n$  stages, one pound of steam will evaporate roughly  $n$  times as

much solvent as in a single-effect unit, but the capital cost of the equipment is considerably increased. Any type of closed evaporator can be adapted to operate on the multiple effect system.

Considering steam-heated evaporators only, there are numerous different types to choose from. The heating tubes may be short or long, vertical, inclined or horizontal, and the steam may be admitted either outside or inside the tubes. By far the commonest type is that having a vertical cylindrical shell, the lower portion of which is divided by two horizontal tube plates situated from 3 to 6 feet apart. The tube plates are connected by a nest of vertical tubes, usually from 1 to 3 inches in diameter, with a single downflow tube of large diameter in the centre. The tubes are filled with sufficient liquid to submerge the upper tube plate, and steam is admitted to the space outside the tubes. This sets up a rapid upward convection of liquid through the small-bore heating tubes, and a corresponding downward circulation through the central downflow. Vapour is withdrawn from a dome on top of the cylindrical shell. This standard type of evaporator is suitable for almost any evaporation process, but particularly for those in which scale or solid is deposited during evaporation. In the case where a solid separates out the evaporator body has a conical bottom with a valve for the removal of the solid. The entire heating element, comprising tube plates, tubes, and steam space, is sometimes called the "Calandria."

Long-tube or so-called "climbing film" evaporators have vertical tubes from 12 to 20 feet in length with steam on the outside. Upward flow of liquid through the tubes is maintained by the air-lift effect of the vapour bubbles. Some types have an external downflow pipe; in others there is no recirculation, and liquid passes through the tubes only once. The latter type is especially suitable where the total time of heating must be short. Long-tube evaporators can achieve high heat transfer coefficients, but they cannot deal with deposited solids unless a special salting-pan is added.

The inclined-tube evaporator with steam outside the tubes can achieve high circulation rates and heat transfer coefficients. It is easily cleaned, and is hence often used for food products. The Yaryan type is a horizontal tube evaporator with steam outside the tubes, which are enclosed in a shell and connected in groups by means of return bends. Liquid is passed through the tubes, partly vaporized, and the vapour and liquid finally separated in a chamber provided with baffle plates. It has been used successfully for strongly foaming liquids.

In forced circulation evaporators, liquid is rapidly circulated through the tubes by means of an external pump. Very high heat transfer coefficients are thus obtained. The system is suitable for viscous liquids, or where expensive materials must be used for the heating surface.

Evaporators having steam inside the tubes are usually of the horizontal-tube type. They are suitable for non-viscous liquids that deposit no salts or scale during evaporation. A similar type may be used for direct heating by means of combustion gases.

An unusual evaporator is the submerged combustion type, in which

a mixture of fuel gas and air is burned directly below the surface of the liquid to be evaporated. It has been used to some extent for sulphuric acid concentration.

A system which theoretically offers multiple-effect economy in a single stage is Thermocompression. Here the vapour from the solution being evaporated is compressed, thus raising its temperature, and the compressed vapour is then used to heat the evaporator. Large heat transfer surfaces are required, as, unless excessive power is used for compression, the temperature difference between vapour and solution is small. The system has been applied to small units for producing distilled water on board ship. With improvements in rotary compressor design, its use may be expected to increase.

*References:* Standard works listed under Chemical Engineering; W. L. Badger, *Heat Transfer and Evaporation* (McGraw-Hill Book Co., New York); E. Hausbrand and B. Heastie, *Evaporating, Condensing and Cooling Apparatus*. (Ernest Benn, London).

**"EVERSOFT" L.D. POWDER** — An approved low-density explosive for use in safety-lamp coal mines.

**"EVIPAN"** — See Hexobarbitone.

**EXOSMOSIS** — See Osmosis.

**EXOTHERMIC COMPOUNDS** — See Heat.

**EXPLOSION RISKS (in Industry)** — See Dusts, and Flash-point.

**EXPLOSIVES** — Explosives are substances which, under the influence of heat or shock, or both, are instantly resolved into gases occupying at the high temperature of explosion comparatively enormous volumes, and consequently exerting tremendous pressure, which may be utilized to disrupt the objective or drive projectiles out of guns. They may consist of bodies such as nitroglycerine and nitrocellulose, which are explosive in themselves, or mixtures of substances which, separately, are non-explosive, but when intimately mixed are capable of being exploded either by ignition or detonation.

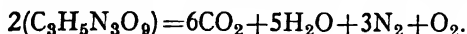
Gunpowder is a mechanical mixture of nitre, or Chile nitre, with charcoal and sulphur in proportions of about 75, 15, and 10 respectively, and is still largely employed for blasting purposes, although it has ceased to be used as a military propellant, or nearly so. The nitre supplies the oxygen necessary for burning up the carbon and the sulphur, at the same time yielding nitrogen gas. It is a so-called "low explosive," while the "high explosives" have a velocity of explosion some 500 times greater. These high explosives are rich in nitrogen, and, when detonated, furnish large quantities of that gas and others which are enormously expanded by the heat generated by the chemical changes which take place, so that they amount to from 10,000 to 15,000 times the volume of the explosive substance itself.

Smokeless powder is the commonly used propellant. It consists, in the case of cordite, of a mixture of high-nitrated gun-cotton, moderated

by gelatinizing by means of acetone, and by incorporating nitroglycerine and "Vaseline." Smokeless powder is not entirely smokeless nor is it a powder. It is manufactured in various shapes, but usually as cylindrical grains (0.085 to 2.170 inches in length and 0.032 to 0.947 inch in diameter) with longitudinal perforations, for small-calibre weapons a single perforation and for large-calibre seven perforations. The grains are shaped by pressing the plastic mixture through steel dies, cutting the extrusion, and then removing and recovering the solvent acetone or ether-alcohol. The pressure exerted by the exploding charge is controlled by (1) the composition of the powder, (2) the shape and (3) the size of the individual grains. Since individual grains burn only on the surface and in layers parallel to that surface, a cord or strip burns with a continually *decreasing* surface until *completely* consumed, but a multi-perforated grain with continually *increasing* surface until *nearly* consumed (single-perforated grains show only slight change of surface during the burning). When the inner and outer webs of a multi-perforated grain have just burned through, a small amount of "slivers" remains, which is either burned in the bore of the weapon or expelled unburned from the muzzle. It is possible to reduce the amount of slivers by shaping the exterior of the cylinder with a scalloped or "rosette" design.

High explosives for blasting and demolition work must burn very rapidly, usually upon detonation (see Detonators). These explosives consist of various substances and mixtures that are designed for the particular purpose in view. For military purposes the most important are trinitrotoluene (TNT), ammonium picrate, picric acid, nitrostarch, tetryl, amatol, and cyclonite. Dynamite and numerous blasting powders are used industrially. Explosives of the gelatine type are chiefly employed in metalliferous mining, all being based upon nitroglycerine. They are plastic, and readily accommodate themselves to irregularities of structure, but they have the defect of being subject to freezing in cold weather. Non-freezing varieties are on the market.

**Nitroglycerol (Nitroglycerine, Glyceryl Trinitrate)** is a pale yellow, odourless, heavy body of oily consistency and sp. gr. 1.6, obtained by the action of strong nitric acid upon glycerol, and is soluble in alcohol and ether. Robertson's apparatus is designed for following its decomposition by the spectroscopic estimation of the evolved nitrogen tetroxide. When decomposed by explosion, the chemical changes that occur are represented by the following equation, from which it will be seen that the whole of the oxygen that is required is self-supplied, and that all the products are gaseous at the temperature of the explosion :



The heat developed by the explosion of 1 gram of nitro-glycerol amounts to 1,459 calories.

Nitroglycerine is used in the preparation of vaso-dilators; its explosives freeze at 8° C., and have to be thawed before use.

**Nitroglycol (Glycol Dinitrate)** ( $\text{C}_2\text{H}_4(\text{NO}_3)_2$ ) is prepared by slowly adding ethylene glycol to a mixture of nitric and sulphuric acids. It

is a colourless, mobile liquid devoid of any appreciable odour, sweetish in taste, of sp. gr. 1.482 at 15° C., and f.p. -20° C. It is finding increasing application as a less sensitive explosive than nitroglycerine, both alone and in admixture with that substance.

**Dynamite** is a mixture of nitroglycerol and the infusorial earth named kieselguhr. It is largely used for blasting purposes, especially in mines.

The velocity of the explosive wave is 6,000 metres per second.

"Blasting gelatine"—a stiff jelly—is the strongest of all nitroglycerine explosives, and other varieties consist of a thin jelly of nitroglycerine thickened with from 3 to 6 per cent. collodion cotton worked up into a plastic mass with suitable proportions of potassium nitrate and wood-meal.

**Trinitrotoluol (T.N.T., Trinitrotoluene)** is obtained by the graduated action of strong nitric acid in the presence of concentrated sulphuric acid upon toluol (toluene), in the form of yellow prismatic crystals of m.p. 81° C., soluble in alcohol and ether but not in water. It has replaced picric acid to a large extent as a filling for shells, exploding with great force when detonated with mercuric fulminate, and being more stable in character and cheaper than picric acid.

**Picric Acid (Trinitrophenol)** is obtained by the graduated action of strong nitric acid in the presence of concentrated sulphuric acid upon carbolic acid (phenol), and is a high explosive. It gives a velocity wave of 7,700 metres per second. Various mixtures of it with *collodion*—a nitrated cellulose prepared from gun-cotton by dissolving the latter in mixtures of ether and alcohol or other solvent—in compressed and molten forms constitute the explosives *melinite* and *lyddite*. Its use was largely superseded during World War I by trinitrotoluene, and by trinitrotoluene mixed with ammonium nitrate.

**Gun-Cotton (Nitrocellulose, Cellulose Nitrate)** (formulated sometimes as  $C_6H_7O_5(NO_2)_3$ , and at others  $C_{12}H_{14}O_{10}(NO_2)_6$ ) is obtained by the graduated action of nitric and sulphuric acids upon cellulose (cotton-waste), several stages of nitration being possible. The sulphuric acid is employed to prevent dilution of the nitric acid by absorption of the water set free during the nitration, and the process is carried on until the product contains about 13.1 per cent. nitrogen. Smokeless gun-powders and most of the violent propellants contain gun-cotton.

Trinitrocellulose is a yellowish, amorphous substance soluble in alcohol, ether, benzol, acetone, amyl acetate, etc.

Dry gun-cotton is one of the most dangerous explosives, as when dry and warm it is very liable to explosion by friction.

The heat developed by the explosion of 1 gram of gun-cotton is 1,010 calories.

"**Amatol**"—A commercial and military explosive made by admixing 20 parts T.N.T. with 80 parts ammonium nitrate, which gradually superseded other high explosives, including picric acid, as a filling for shells during World War I, as, although less rapid and shattering than T.N.T., it gives greater flame, is cheaper, and practically smokeless, due to the excess of oxygen provided by the ammonium nitrate,

the ideal proportions to produce complete combustion being given by the equation :



"**Ammonal**" — An explosive of the ammonium nitrate class, resembles amatol, but containing finely divided aluminium in admixture.

"**Blastine**" is an explosive of the chlorate type.

"**Cheddite**" is an explosive, the chief ingredient of which is potassium chlorate, made up with proportions of nitronaphthalene or dinitrotoluene and from 5 to 6 per cent. castor oil.

"**Cordite**" is an important military propellant, and is a mixture of gun-cotton and nitroglycerine dissolved in acetone, and thickened and rendered more stable with about 5 per cent. of "Vaseline". The excess of acetone is afterwards evaporated off from the gelatinous mass, which is prepared in cord form.

"**Cyclonite**" ("**Hexogen**," "**R.D.X.**" "**T4**") is *cyclo*-trimethylene-trinitramine ( $\text{CH}_2\text{N}(\text{NO}_2)_3$ ), a military explosive, which is described as a fine white crystalline (rhombic) substance ; odourless, tasteless, non-toxic, non-hygroscopic, and not affected by light or warm humid air ; of m.p.  $202^\circ\text{C}$ . with decomposition, when heated quickly to  $280^\circ\text{C}$ . explodes violently ; insoluble in water (at  $100^\circ\text{C}$ . 0.15 per cent.), sparingly soluble in most organic solvents, except soluble in acetic acid, hot formic acid, or acetone (at  $20^\circ\text{C}$ . 5 parts per 100 parts acetone, at  $56^\circ\text{C}$ . 10 parts) ; not affected by dilute alkalis, but reacts with hot concentrated alkalis and with concentrated sulphuric acid. The accompanying table comparing some of the properties of "Cyclonite" and T.N.T. makes it evident that the former is a blasting explosive of high intensity. For structural demolition, and in mines and projectile bombs "Cyclonite" is a favoured explosive, and it is also used as a propellant when mixed with paraffin wax or with gun-cotton and moderated with various nitro-aromatic compounds. "Cyclonite" is

TABLE SHOWING SOME CHARACTERISTICS OF "CYCLONITE" AND T.N.T.

Characteristic	"Cyclonite"	T.N.T.
Density, grams per c.c. . . . .	1.70	1.58
Velocity of detonation, metres per sec. . . . .	8,380	6,700
Gas evolved on detonation, standard litres per kg.	908	690
Lead block (Trauzl) expansion test, ml. . . . .	520	310
Compression (Kast) test, mm. . . . .	5.2	3.6
Figure of insensitivity (Berthe, 2 kg. weight), cm. (picric acid 60 cm.) . . . . .	42	80
Heat of explosion, calories per gram . . . . .	1,290	3,600

manufactured by the nitration of hexamethylenetetramine ( $(\text{CH}_2)_6\text{N}_4$ ) using nitric acid of 95 to 100 per cent. strength, and maintaining a temperature below  $30^\circ\text{C}$ . The yield is about 70 per cent. of theoretical.

$$\begin{array}{c}
 \text{N} \\
 \diagup \quad \diagdown \\
 \text{CH}_2 \quad \text{CH}_2 \\
 \diagdown \quad \diagup \\
 \text{N} \\
 \diagup \quad \diagdown \\
 \text{CH}_2 \quad \text{CH}_2 \\
 \diagdown \quad \diagup \\
 \text{N} \\
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 \text{CH}_2 \quad \text{CH}_2 \\
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 \text{CH}_2 \quad \text{CH}_2 \\
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 \text{N} \\
 \diagup \quad \diagdown \\
 \text{CH}_2 \quad \text{CH}_2 \\
 \diagdown \quad \diagup \\
 \text{N}
 \end{array}
 + 4\text{HNO}_3 + 2\text{NH}_4\text{NO}_3 + 6(\text{CH}_3\text{CO})_2\text{O} \rightarrow$$

Hexamethylenetetramine

$$2 \left( \begin{array}{c} \text{N}-\text{NO}_3 \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{O}_2\text{N}-\text{N}-\text{CH}_2-\text{N}-\text{NO}_2 \\ \text{"Cyclonite"} \end{array} \right) + 12\text{CH}_3\text{COOH}$$

Nitroglycerine	..	..	..	9 to 11 parts
Ammonium nitrate	..	..	..	48 „ 51 „
Sodium nitrate	..	..	..	8 „ 10 „
Ammonium oxalate	..	..	..	17 „ 19 „
Wood-meal (dry at 100° C.)	..	..	..	11 „ 13 „
Moisture	..	..	..	2 „

## EXPLOSIVES

## "Capexco"

Nitroglycerine	..	..	..	32	to 34	parts
Nitrocellulose	..	..	..	0.5	„	1.5 „
Sodium nitrate	..	..	..	24	„	25 „
Ammonium oxalate	..	..	..	30	„	32 „
Wood-meal (dry at 100° C.)	..	..	..	8	„	10 „
Moisture	..	..	..	..	2	„

## "Celmonite"

Ammonium nitrate	..	..	..	65.5	to 68.5	parts
Trinitrotoluol	..	..	..	10.5	„	12.5 „
Sodium chloride	..	..	..	19.5	„	21.5 „
Moisture	..	..	..	..	2	„

## "Ligdynite"

Nitroglycerine	..	..	..	25	to 27	parts
Sodium nitrate	..	..	..	27	„	29 „
Sodium chloride	..	..	..	10	„	12 „
Wood-meal (dry at 100° C.)	..	..	..	30	„	33 „
Moisture	..	..	..	2	„	4.5 „

## "Superligdynite"

Nitroglycerine	..	..	..	15	to 17	parts
Ammonium nitrate	..	..	..	15	„	17 „
Sodium nitrate	..	..	..	23	„	25 „
Flour (dry at 100° C.)	..	..	..	10	„	12 „
Wood-meal (dry at 100° C.)	..	..	..	19	„	21 „
Sodium chloride	..	..	..	9	„	11 „
Moisture	..	..	..	2	„	4 „

References: C. A. Woodbury and W. C. Holmes on "Commercial Explosives Industry" (*Ind. Eng. Chem.*, **27**, 632 (1935)); H.M. Inspectors' Annual Reports of Explosives (H.M. Stationery Office); *Explosives*, by E. de Barry Barnett (Baillière, Tindall and Cox, London); *Explosives. Their History, Manufacture, Properties, and Tests*, by A. Marshall (J. and A. Churchill, London); *The Modern High Explosives*, by M. Eissler (John Wiley and Sons, New York); *Nitro-Glycerine and Nitro-Glycerine Explosives*, by P. Nasum (Baillière, Tindall and Cox, London); *The Rise and Progress of the British Explosives Industry*, 7th International Congress of Applied Chemistry, 1907; U.S. Production of Explosives, Data by U.S. Bureau of Mines; William Macnab on "Chemical Engineering in Explosives Manufacture" (*Trans. Inst. Chem. Eng.*, **13**, 9 (1935)); T. L. Davis on *The Chemistry of Powder and Explosives* (John Wiley and Sons, New York); Jules Bebie on *Manual of Explosives, Military Pyrotechnics, and Chemical Warfare Agents* (Macmillan, New York); H. B. Faber on *Military Pyrotechnics*, 3 vol., 1920; "Bobbinites," Detonators, and "Eversoft."

**EXTRACTION** usually refers to Solvent Extraction, that is, the treatment of a substance with a liquid solvent which dissolves out certain constituents and leaves others behind. Sometimes the term is loosely extended to the expression of oil from oil-seeds and similar processes. In the laboratory, solid substances are often extracted by boiling with solvent under a reflux condenser, cooling, and filtering off the extract. In the Soxhlet apparatus the substance is continually treated with freshly condensed solvent, whereby the soluble constituents are more completely removed than when immersed in the extract itself.

Industrial extraction operations fall into two main classes according as the material to be treated is solid or liquid. Either type of process can be carried out batch-wise or continuously, and with either concurrent or countercurrent flow of solvent. Countercurrent processes effect the maximum degree of extraction with the minimum amount of solvent.

The method used to extract *solids* depends on whether they are coarse or fine. Finely divided solids may be suspended and agitated in the solvent by means of paddle mixers, propeller mixers, or air agitation until solution is complete. The suspension is then passed to a tank where the solid residue settles out and the clear extract is withdrawn. Examples of such processes are the extraction of gold-bearing ore with cyanide solutions, and the separation and recovery of sodium hydroxide solution from calcium carbonate precipitate. The operation may be made continuous by using mechanical settling devices such as the Dorr Thickener. If countercurrent operation is required the material is treated in stages, fresh solid material meeting partly saturated solvent, and the insoluble residue contacting fresh solvent before being discarded.

Coarse lumps or fibrous material are usually extracted in stationary tanks through which the solvent is circulated. This operation is also called Lixivation or Leaching. The Shanks system employs a battery of tanks through which the solvent passes in series. These tanks are charged and emptied in succession, and the points of entry and withdrawal of liquid are correspondingly changed so that fresh solvent always enters at a tank containing residue that is almost exhausted, proceeds to other tanks of material that is progressively fresher, and finally leaves after passing through a fresh charge. The operation is thus countercurrent. Tank leaching is used for such differing materials as tan bark, sugar beet, copper ores, and Chilean nitrate. In the sugar beet industry, continuous leachers have been used in which the solids are propelled through a trough by means of a helix.

The extraction of *liquids* by immiscible solvents is often performed in equipment similar to that used for finely divided solids. The essential components are an agitator in which the liquids are thoroughly mixed, and a tank in which they are allowed to settle into two layers that are separately drawn off. One quite effective method of mixing is to circulate the two liquids through a centrifugal pump. Alternatively they may be pumped together through a column containing orifices or baffle plates, or through a coil of pipe sufficiently long to give

the required contact time. Settling tanks should provide a relatively large liquid-liquid interface and small depth of liquid on either side of the interface. A common form is the horizontal or inclined cylinder. Liquid-liquid settlers are often provided with an interfacial level controller which regulates the discharge of the denser liquid. The mixing and settling system may be made approximately countercurrent by having several stages through which the two liquids pass in opposite directions.

The foregoing methods of extraction in stages are only approximately countercurrent; within each stage, the flow of solvent and charge is concurrent. True countercurrent extraction is effected in towers in which the denser liquid is charged at the top and leaves at the bottom, while the lighter liquid enters at the bottom and leaves at the top. One of the two liquids is dispersed into droplets by a perforated spray. If the denser liquid is dispersed, the droplets fall by gravity through a rising current of lighter liquid; if the latter is dispersed, droplets of lighter liquid rise through the denser. Countercurrent extraction towers may be empty (so-called "spray towers"), but they are usually charged with packing to create turbulence and promote contact between the two liquid phases. Packed towers are much used in the solvent extraction of lubricating oils, and it seems likely that they will tend to replace stagewise methods in other fields.

In the design of countercurrent extraction towers, the number of Theoretical Stages needed to effect the desired degree of extraction is calculated, and the permissible liquid velocities determined by experiment, also the height of packing equivalent to a Theoretical Stage (H.E.T.S.). A more theoretically correct, but somewhat less convenient method of calculation uses the Transfer Unit (H.T.U.) concept instead of the Theoretical Stage. The H.E.T.S. or H.T.U. varies considerably with liquid velocity; in general, it diminishes with increasing velocities up to the flooding point. Towers are therefore most efficient when operating near their maximum capacity. The flooding point is reached when one phase begins to be carried along with the other instead of moving against it, so that one of the leaving streams is contaminated with the other liquid.

The following practical conclusions have resulted from studies on countercurrent extraction: (1) Raschig rings appear to be more effective than other types of packing. (2) Smaller rings give lower H.E.T.S. values (more efficient extraction), and also lower flooding velocities (less throughput for a given cross-section) than larger rings. (3) When the two liquids are charged in unequal proportions, the larger streams should generally be dispersed in the smaller, thus creating more droplets and a larger interface than when the smaller stream is dispersed. (4) There is some evidence that efficiencies may be better if the dispersed phase does not wet the packing or the tower wall.

Where the two liquids are partly miscible, more complete extraction is attained by recycling a proportion of one or both liquids as reflux or "backwash." The operation is then analogous to Fractional Distillation.

Solvent extraction is commonly practised to secure certain vegetable drugs, such as caffeine from tea leaves, vanillin from vanilla beans, and atropine from belladonna; also in the refining of petroleum lubricating oils to improve the viscosity-temperature coefficient, the stability against oxidation, and to lower the carbon residue. (See Solvents.)

*References:* Standard works listed under Chemical Engineering; T. K. Sherwood, *Absorption and Extraction* (McGraw-Hill Book Co., New York); M. B. Donald, *Trans. Inst. Chem. Eng.* (London), **15**, 77 (1937); numerous papers in the *Trans. Am. Inst. Chem. Engrs.*; Symposia on "Absorption and Extraction" in *Ind. Eng. Chem.*, **29**, 309 (1937); **42**, 1021 (1950).

**EXTRACTIVE METALLURGY** — See Process Metallurgy.

**EXTRACTS** — Concentrated preparations obtained by extracting vegetable drugs with solvents, usually aqueous alcohol, and evaporating the solution to dryness and powdering (dry extracts) or to a specified volume (liquid extracts). Extracts of drugs containing a potent substance, such as atropine in belladonna, are standardized to contain a specified amount of active principle. (See Extraction.)

**FABRICS** — See Textiles.

**"FABRIKOID"** (Du Pont) — Trade-mark for pyroxylin coated and impregnated fabrics widely used for furniture upholstery, luggage, shoes, and bookbinding.

**"FABRILITE"** (Du Pont) — Trade-mark for vinyl resin coated fabrics. Used for tablecloths, handbags, luggage, and in upholstery.

**"FACTOCRETE"** — A material compounded of chemically treated wood fibre, Portland cement, and other substances, prepared under great pressure, and used in the construction of dwellings; said to be two-thirds of the weight of concrete, and equally strong; mouldable to any shape.

**FADEOMETER** — An apparatus designed to test the fastness of dyes, inks, paints, etc., to light, in which the light used is the carbon arc, being of uniform quality and intensity, unlike sunlight, which varies so much in power at different times and places. In case of dyed fabrics, exposure of one hour in the fadeometer is stated to have the same fading effects as 1.3 hours' exposure to June sunlight.

**FAHRENHEIT** — See Heat.

**FANNING EQUATION** — See Fluid Dynamics.

**FARADAY** — See Electricity.

**FARINA** — Finely ground cereal or starchy materials, used in breakfast foods, and baked goods. Specifically, the name farina is usually applied to uniformly sized particles of wheat endosperm used in cooked breakfast foods and macaroni products.

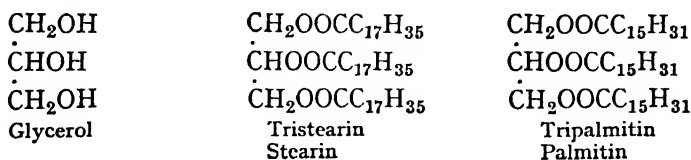
**FAT HARDENING** — See Hydrogen (Hydrogenation).

**FATS** — Most animal and vegetable fats, including suet, tallow, butter, and many of the various fish and nut oils, are mixtures of distinct fats or substances chemically termed triglycerides or "glyceryl esters," of stearic, palmitic, oleic, and other acids. These fats are the particular esters which react with acids (and bases) to yield glycerol and the named fatty acids (and their salts when bases are used). Stearic and palmitic acids are solids, and oleic acid fluid in their separate forms, the consistence of a fat or oil depends upon the relative proportion of these several fat constituents named individually stearin, palmitin, olein, etc. The fats all melt well below 100° C., and are all saponifiable, yielding as described glycerol and salts, which are also soaps. (See Saponification.)

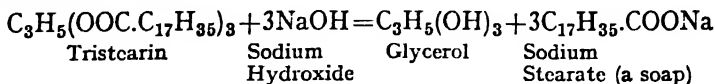
Tristearin as isolated from beef-fat is reported to melt at 71.2° C., and to have a sap. v. 189.6. Lard does not contain tristearin.

Information respecting the manner in which the fatty acids are combined with glycerol in natural fats is incomplete. The investigations of Hilditch and his associates have disclosed some differentiation between the constitution of animal and vegetable fats; seed or kernel fats, for example, show a tendency for all the fatty acids to be linked with glycerol in a more even distribution than occurs in animal fats. Their methods of research in this and other directions and the results thereof are described in various papers. There is evidence that carbohydrates constitute an intermediate stage in vegetable fat metabolism and some inconstancy of composition in the fats themselves, and these methods of investigation have so far given a more satisfactory picture of the substances concerned.

The constitution of fat is illustrated by showing the constitutional formulas of glycerol and stearin and palmitin side by side :



When stearin is saponified with sodium hydroxide, the following change takes place :



A number of fatty acids have been synthesized and some result from the oxidation of paraffin wax (see Oxo Reaction).

The manufacture of hardened fats is dealt with under the heading of Hydrogen (Hydrogenation).

Fats and fatty acids are largely used in the manufacture of soaps, candles, foodstuffs, and margarine; tallow and bone-fat and some oils are used in connection with the sizing of certain textiles to soften the effect of starch; whilst nut and fish oils have in recent years acquired growing importance on account of the ever-increasing demand for margarine. "Stearine" candles consist for the most part of stearic acid, some proportion of paraffin or other wax being added to prevent crystallization. The stearic acid is obtained by hydrolysis of the beef and mutton fats with either superheated steam, or dilute sulphuric acid, or lime and water. When steam is used, the glycerol distils over with the steam, the fatty acids being left behind. In the "acid process" they are boiled with strong sulphuric acid, while the "fermentation process" depends upon the lipolytic action of certain enzymes, such as those contained in castor seed.

The "Twitchell" process of hydrolysing fats so as to obtain glycerol and fatty acids directly, without the use of alkalis or by heating under pressure, employs a fatty aromatic sulphonic acid as a reagent—for example, that obtained by allowing an excess of sulphuric acid to act on a solution of oleic acid dissolved in an aromatic hydrocarbon, such as benzene or naphthalene. According to one account, the constitution of Twitchell's reagent is  $C_{18}H_{35}O_2.C_{10}H_8SO_3H$ . The cleansed fat or oil is mixed with from 40 to 50 per cent. of distilled water containing about 2 per cent. of the reagent, and the mixture kept stirred and heated by means of an open steam coil for from ten to fifty hours, according to the nature of the fat. At the conclusion of the process, the underneath layer contains all the glycerol in water solution, and the upper layer contains the free fatty acids thus rendered available for soap-making or disposal otherwise. (See "Zinc Formosul.") According to one account, 75 c.c. of concentrated sulphuric acid and a mixture of 50 grams fat acids from rape oil, with 17 grams of phenol, is reported to give good results as a "Twitchell" reagent.

In comparative tests made by O. Steiner, the "contact" reagent, the "Pfeilring" reagent, and a reagent prepared from lignite tar hydrocarbons for the hydrolysis of fats and oils, a mixture of 100 grams pure linseed oil, 0.5 gram of reagent, enough sulphuric acid to yield 0.2 gram of  $H_2SO_4$ , and 50 grams of water, were boiled under a reflux condenser. After fifteen hours the effected hydrolysis was 85.9, 85.5, 76.7, and 77.2 per cent. with the "contact," "lignite tar," "Twitchell," and "Pfeilring" reagents respectively. It is known that a wide range of substances possess fat-splitting properties, but it appears essential they should be strongly acidic, well sulphonated, and soluble in both fat and water.

The autoclave process of hydrolysis consists in exposing the charge of oil in an autoclave to steam from a high-pressure boiler in presence of a certain percentage (about  $2\frac{1}{2}$ ) of lime or magnesia at 8 atmospheres pressure, thus splitting up the fats directly into fatty acids and glycerol. Resort is made to this process in order to obtain a lighter colour of

fatty acids than is obtained by other processes, and to effect their separation into solid and liquid fractions. The higher the iodine values of the products, the greater is the amount of solid isomerides of oleic acid formed, and the greater the percentage of pitch left behind.

All fats and oils contain more or less acids more unsaturated than oleic, which leads to the production during distillation of *iso*-oleic acid, and the more of this there is in the product, the more greasy is the stearin obtained.

The candle-maker requires a distillate which is crystalline when cold, and the adulteration of tallow with wool fat gives a distillate which crystallizes imperfectly, and so will not press satisfactorily. Cold-pressed stearins of 100 per cent. free fatty acids are produced commercially.

Attempts have been made to produce edible fats from certain alcohols, and using isopropyl alcohol esterified with stearic acid, a good yield of isopropyl stearic ester can be obtained of m.p. 24° C., said to be of a mild flavour suitable for use as an edible fat. Churned with tallow and milk it makes, so it is stated, a margarine useful for pastry-making.

When heated to from 250° to 300° C., fats and oils are decomposed, acrolein being among the products.

As a general statement, **rancidity** in fats and oils may be said to result from chemical changes brought about by micro-organisms or their enzymes in the presence of air, light, and moisture. It is regarded by some as resulting from bacterial action on the glycerides, but by others as due, in the first place, to the formation of superoxides of the unsaturated glycerides and their subsequent decomposition (attended with the production of aldehydes and aldoacids). In presence of air or oxygen, metals accelerate rancidity in lard, maize, and cotton-seed oils, and light is essential, or at least greatly promotes the process of rancidity in oils and fats so exposed. Slight hydrogenation improves the quality of lard by increasing the resistance to attack by oxygen (*Chem. and Ind.*, **51**, 148 (1932)). The appearance of moulds is accompanied by a marked increase in free fatty acidity, and it seems probable that the presence of free oleic acid is an active factor in rancidity, and acrolein decomposition products are always found in fully rancid oils. In general, rancidity is accompanied by a fall in specific gravity, increase in "Reichert-Meissl," "Polenské," and acid values, and a decrease in iodine value.

*References*: "Antioxidants and the Autoxidation of Fats," by L. A. Hamilton and H. S. Olcott (*Ind Eng. Chem.*, **29**, 217 (1937)); "The Alcoholysis and Hydrolysis of Fats," by G. K. Rowe (*J.S.C.I.*, **52**, 49 T (1933)); "The Action of Light on Fats," by C. H. Lea (*J.S.C.I.*, **52**, 146 T (1933)); *Vegetable Fats and Oils*, by G. S. Jamieson (Reinhold Publishing Corp., New York); *Industrial Chemistry of Fats and Waxes*, by T. P. Hilditch (Baillière, Tindall and Cox, London); *Fats: Natural and Synthetic*, by Myddleton and Barry (E. Benn, Ltd., London); *Oils, Fats, and Waxes*, by P. J. Fryer and F. E. Weston

(Cambridge University Press); *Industrial Oil and Fat Products*, by A. E. Bailey (Interscience Publishers, New York); *Fats and Oils. An Outline of their Chemistry and Technology*, by H. G. Kirschenbauer (Reinhold Publishing Corp., New York); *The Chemical Constitution of Natural Fats*, by T. P. Hilditch (John Wiley and Sons, New York); Glycerol, Hydrogenation, Margarine, Oils, Soaps, Tallow, Waxes.

The following are important tests in connection with the examination and valuation of fats and oils:

**Acetyl Value of Fats (Acet. v.)** — This shows the amount of hydroxy-acids present, is represented by the number of milligrams of potassium hydroxide required to neutralize the acetic acid resulting from the hydrolysis of 1 gram of acetylated fat or wax, and is a measure of the number of hydroxyl groups present. A published formula is as follows:

$$A = \frac{S' - S}{1 - 0.00075S}$$

where  $S$  is the neutral hydrolysis value before acetylation and  $S'$  the value after acetylation.

**Acid Value (Acid v.) of Fats** — This is the number of milligrams of potassium hydroxide required to neutralize the free fatty acids contained in 1 gram of fat. The value is principally a measure of rancidity.

**Fat Extraction** — See Extraction.

**Hehner Value** (of fats, oils, and waxes) represents the percentage of insoluble fatty acids *plus* the non-saponifiable constituents.

**Iodine Value (i. v.) (Hübl Number) of Oils and Fats** — This determination, as commonly performed on samples of oils, fats, and waxes, is used to indicate the degree of unsaturation of the compound—that is, the number of pairs of carbon atoms in which two (or in some cases three) valency bonds are concentrated between the two carbon atoms. Any such double (or treble) linkage is in a state of strain, and when the substance containing it comes in contact with certain other substances (*e.g.*, the halogens), one of the bonds breaks and two atoms of the new substance are attached, one to each of the carbon atoms originally joined by the double linkage. Thus, every two atoms of the reagent absorbed represent one double linkage in the original substance. The saturated fatty acids have an iodine value of zero, as have also the paraffin hydrocarbon oils.

The reagent used in the Hübl or Wijs method—a modification of the Hübl process—is iodine monochloride (ICl), which adds on one atom of iodine to the one carbon atom, and one atom of chlorine to the other carbon atom. Thus in this case, *one* atom of iodine absorbed indicates the presence of one double linkage. The method of Hübl is to make up an iodine monochloride solution from iodine and mercuric chloride, and add excess of this to a known weight of the fat or oil dissolved in chloroform. After standing for some time, the excess of iodine chloride is estimated by the potassium iodide and thiosulphate method; a blank test is carried out alongside, using an equal quantity of the

reagent without the substance, and the difference indicates the amount of iodine absorbed by the substance. In Wijs' method an acetic acid solution of iodine chloride is employed, and the Hanus method an acetic acid solution of iodine monobromide.

The iodine value may be defined as the amount of iodine chloride absorbed by 100 grams of the substance expressed in terms of iodine, and is a measure of the proportion of unsaturated fatty acids which in their free state or combined with glycerol react with the halogens, and thus form saturated compounds.

The iodine value does not invariably give a satisfactory measure of the relative value of fatty oils for practical purposes, differences being observable, for example, in the case of unsaturated fatty acids, and L. A. Jordan doubts the validity of the iodine test as the sole criterion of quality for drying oils and thinks the true degree of unsaturation of oils could possibly be best obtained by hydrogenation.

The drying properties of oils are in almost direct ratio of their iodine values, thus linseed (drying) oil has iodine number from 170 to 204, hempseed (semi-drying) oil from 141 to 148 (of the order of 150), and arachis (peanut) (non-drying) oil of 85.

**Neutralization Equivalent** is the number of grams of the sample neutralized by *one litre of normal alkali*. This number, therefore, is equal to the *equivalent* weight of a pure acid.

**Polenski (or Polenské) Value** is the difference in temperature between the melting and solidification points of fats.

**Refractivity** of oils and fats is ordinarily determined by use of the Abbé-Zeiss or Fery instrument, using sodium light at 20° C.

**Reichert-Wollny (Reichert-Meissl) Fat Value** — The values of the soluble, *volatile*, fatty acids contained in fats, represented by the amount of alkali, that is, the number of cubic centimetres of  $\frac{N}{10}$  potassium hydroxide solution (or  $\frac{N}{10}$  barium hydroxide solution) required to neutralize them, as obtained from 5 grams of fat by saponification with alcoholic sodium hydroxide, evaporation of the alcohol, treatment of the residue with dilute sulphuric acid, followed by distillation and titration of the distillate.

**Saponification Equivalent** is the number of grams of the sample saponified by *one litre of normal alkali*. This number, therefore, is equal to the *equivalent* weight of a pure ester.

**Saponification Value (Sap. v.) (Sap. number)** of fats and oils indicates the number of milligrams of potassium hydroxide required for the complete saponification of 1 gram of an oil or fat. The presence of free fatty acids increases the saponification values.

**Unsap. Matter** — This is the percentage of ether-soluble material remaining after complete saponification, and consists chiefly of sterols and allied substances in pure oils and of petroleum or other hydrocarbons if adulterated.

**FATTY ACIDS** — See Acids, and Fats.

"**FECULOSE**" is an acetylated starchy product produced by treating dry starch with glacial acetic acid at 120° C., using, if desired, small additions of mineral acids or formic acid as accelerators. It differs from starch in properties, in that, upon heating with water, it gives a clear stable solution which sets to a soft, translucent, gelatinous mass, forming an excellent substitute for gelatine and gums and is used as a dressing in the textile industry, and for sizing paper.

**FEEDING STUFFS**, as used by farmers, depend for their value upon certain digestible constituents, such as oil or fat, albuminoids, carbohydrates, and mineral salts, the unassimilable parts having only, when used as manure, a certain fertilizing value. The heat value of one part fat is about equal to that of 2·4 parts starch or 2·5 parts sugar, but the muscular system of animals is only sustainable by the nitrogenous or albuminoid constituents of foodstuffs, and these are calculated by multiplying the protein nitrogen content by 6·25. The mineral constituents—mainly phosphates of potash and calcium—are also essential items of food. The water content has no feeding value. The vitamin principles of vegetables and fruits are of corresponding value to animals as to human beings. Home-grown crops, such as pasture grass, hay, straw, swedes, and mangolds, form the basis of all foods, but have to be supplemented by the use of more concentrated food, such as linseed, cotton, rape, and other seed cakes, maize, beans, bran, oats, and barley.

The following analytical figures are abstracted, by permission, from a paper by Alfred Smetham and F. Robertson Dodd, published in the Royal Lancashire Agricultural Society's annual journal for 1921 :

	Water	Oil	Albuminoids or Proteins	Digestible Carbohydrates	Woody Fibre	Mineral Matter
Meadow grass .. ..	70·48	0·83	2·95	14·14	9·54	2·06
Meadow hay .. ..	14·30	1·48	9·32	41·28	26·83	6·79
Wheat straw .. ..	13·81	1·47	2·96	36·29	47·07	4·40
Swedes .. ..	90·42	0·20	0·91	6·61	1·29	0·57
Mangolds .. ..	87·89	0·17	1·32	8·63	1·06	0·93
Linseed cake, according to variety, from ..	9·25-12	6-13	28-37	27-41	6-14	5-7
Cotton-seed cake, according to variety, from ..	9-11	13-24	18-22	22-31	17-27	3·5-5
Maize, according to variety, from ..	12-17	4-5	9-10	66-70	1-2	1½-1¾
Beans (English) ..	14·14	1·86	28·12	46·70	6·14	3·04
Bran .. ..	11·45	4·33	16·46	57·00	6·50	4·25
Oats (crushed) ..	13·45	6·77	11·12	56·92	9·14	2·60
Barley (grain) ..	14·95	1·46	8·59	67·96	4·46	2·58

In a later communication, Messrs. Smetham and Dodd give tables showing the standard rations required per day for every 1,000 pounds of live weight of cattle and the calculated "food units" of many cereals and by-products, these values being calculated on the assumption that

oil and albuminoids are of equal value and together are  $2\frac{1}{2}$  times as valuable as the carbohydrates (same journal, 1928).

In a lecture by G. H. Ayers, the "digestible food units" of certain products, calculated upon the albuminoid matter, the oil and fat, and the carbohydrate constituents, have been given as follows :

Meat meal .. ..	190-204	Distillers' grains (dried) ..	101
Bone and meat meal ..	140-165	Palm-kernel cake ..	96
Bone meal .. ..	95-105	Wheat sharps .. ..	90.5
Dried blood .. ..	190-204	Maize meal .. ..	86.5
Swill or plate leavings	120-134	Brewers' grains (dried) ..	84.5
Fish meal .. ..	150-170	Barley .. ..	83
Ground-nut cake ..	145	Wheat bran .. ..	77.5
Decorticated cotton-cake	126	English oats .. ..	75.4
Soya-bean cake .. ..	122	Malt culms .. ..	69.9
Linseed cake .. ..	120		

Fish-meal (for the preparation of which many types of plant exist) contains from 8 to 10 per cent. oil and from 45 to 50 per cent. albuminoids, and is therefore used as a valuable feeding stuff for cattle, pigs, and poultry, also as a good fertilizer.

In a process devised by F. Bergius for the utilization of wood in the preparation of a cattle-feed stock, the cellulose is converted into a kind of sugar by use of hydrochloric acid in a special manner, and this, mixed with dried potato flakes, is said to provide a suitable feed-stock to which protein can be added in the form of soya-bean meal or oil cake. (See Ensilage, Oil Cakes, and Vitamins.)

**FEHLING'S SOLUTION**—A solution of cupric sulphate mixed with Rochelle salt (a double tartrate of potassium and sodium) and alkali, used as an oxidizing agent, and employed as a test for the determination of inverted sugars or other reducing agents in solution, by ascertaining the amount of cuprous oxide produced by its action. A strength recommended by one writer is that of which 10 c.c. are equivalent to 0.05 gram of dextrose.

Sucrose, common sugar, does not reduce Fehling's solution, and requires to be first of all inverted.

**FELDSPARS (FELSPARS)** (Crystal systems Nos. 5 and 6)—Various compound mineral silicates of aluminium and other metals, found abundantly in nature, and widely distributed, including many large deposits in Cornwall, Ireland, Wales, and Scotland, and in Maine, Massachusetts, Connecticut, and New York, U.S.A., as high as 14 per cent. potassium oxide ( $K_2O$ ) being obtainable from some small veins of *orthoclase* or *potash felspar* ( $K_2O, Al_2O_3, 6SiO_2$ ), although most of them are not suitable for potash extraction. The silica content varies in the more important sorts from 43 to about 69 per cent. Feldspar is used in the enamel, glass, pottery, and porcelain manufactures. (See Clays, Basalt, Porcelain, and Potassium.)

FELDSPAR, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country	Feldspar Metric Tons
Sweden .. .. .	45,000
Czechoslovakia .. .. .	30,000*
Norway .. .. .	28,000
Italy .. .. .	13,100
Germany .. .. .	10,600
Finland .. .. .	4,600
Rumania .. .. .	2,100
	<hr/>
	133,400
U.S.A. .. .. .	243,200
Canada .. .. .	14,500
	<hr/>
	257,700
Argentina .. .. .	1,000
British India .. .. .	600
Australia .. .. .	3,900
	<hr/>
Sum of above .. .. .	396,600

WORLD PRODUCTION, approximately the above.

\* Estimated.

**FELT** — Wool or hair worked into sheet form by matting. (See Fibres, and Hair.)

**FENCHENE** — A terpene ( $C_{10}H_{16}$ ) of sp. gr. 0.869 and b.p. 150° C.

**FENCHONE** — A ketone ( $C_{10}H_{16}O$ ) of sp. gr. 0.944 and b.p. 195° C., and a constituent of thuja oil and fennel-seed oil.

**FENNEL, OIL OF** — A colourless or pale yellow essential oil obtained by distillation from the fruit of *Faniculum vulgare*, containing fenchone ( $C_{10}H_{16}O$ ), a dextro-rotatory ketone isomeric with camphor, and anethole (80 to 90 per cent. in some samples), together with pinene, dipentene, and phellandrene. It is soluble in alcohol and ether and is used in perfumery and in making liqueurs. The herb is cultivated in many European countries, India, Japan, and Persia; but the Saxony and Galician varieties yield most oil (about 4 to 6 per cent.); sp. gr. 0.960 to 1.000 at 15° C.; ref. ind. 1.525 to 1.550 at 20° C.; opt. rot. +4° to +24° at 20° C. The East Indian variety (*Fæniculum pammorium*) yields only about 2 per cent. of oil.

**FENUGREEK** — See Fœnugreek.

**FERBAM (Ferric Dimethyldithiocarbamate)** — A fungicide.

**FERGUSONITE** — A mineral represented as  $Y(Cb,Ta)O_4$ , of crystal system No. 2, and sp. gr. 5.8, with which uranium is also found in association.

“**FERMATE**” (Du Pont) — Trade-mark for ferric dimethyldithiocarbamate, used as a fungicide for the control of apple and pear scab, brown rot, fruit rot, and blue mould on tobacco.

**FERMENTATIONS** — Chemical changes brought about by yeast and other forms of cell life (including bacteria and various fungi) in suitable media, but directly due to enzymes, which are produced by or contained in the living cells. The act of fermentation is generally accompanied with liberation of gas (effervescence) and the evolution of heat.

Yeast cells (*saccharomyces*), for example, and an extract prepared from them but free from the living cells, contain zymase, an enzyme which breaks up certain sugars to the extent of about 95 per cent. into alcohol and carbon dioxide:  $C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$ . A medicinal preparation known as "zymine" is made by the extraction of moist yeast cells with acetone, and, while it is quite incapable of growth or reproduction, it is much more active in inducing fermentation than they are. The most favourable temperature for fermentation is from 25° to 30° C., and living yeast cells are killed when the alcoholic strength of the product reaches about 14 per cent.

The lactic fermentation or souring of milk is induced by a bacterium known as the *Bacterium lactis*, but if a mixed fermentative agent is employed, such as old cheese, which contains many kinds of ferment, the lactic acid first of all produced is changed into butyric acid.

In the butyric fermentation of starch or sugar induced by the *Bacillus butyricus*, butyric acid is produced.

The change of alcohol into acetic acid experienced in the souring of light wines or beer, is another act of fermentation due to enzymes.

The fermentation of starch by the action of *Clostridium acetobutylicum* (Weizmann), which normally produces butyl alcohol, acetone and ethyl alcohol in a fixed ratio, is referred to under the heading of Acetone. This is an illustration of the possibility of modifying the ratio of the products by alteration of the conditions of nutrition of organisms.

In industries dependent upon processes of fermentation, great care has to be taken in the preparation of pure cultures of the organisms required, so as to avoid the formation of undesirable products which might result from the action of foreign or pathogenic organisms, thus reducing the yield and imparting damaging qualities.

**References :** A survey of fermentation processes in connection with the making of bread, tea, coffee, cocoa, sauerkraut, pickles, vinegar, sauces, cheeses, etc., by F. C. Black (*Ind. Eng. Chem.*, **22**, 1166 (1930)); article on "Fermentation Phenomena," by T. K. Walker (*Chem. and Ind.*, **49**, 946 (1930)); "Some Fermentative Changes of Technical Interest," by F. Challenger (*Ind. Chem.*, **6**, 97 (1930)); "Cellulose Fermentation," by H. Langwell (*Chem. and Ind.*, **51**, 988 (1932)); "Recent Advances in the Fermentation Industries," by J. V. Eyre (Lecture, Institute of Chemistry, November, 1931); *Micro-organisms and Fermentation*, by A. Jörgensen (C. Griffin and Co., London); *The Problem of Fermentation*, by M. Schoen, translated by H. L. Hind (Chapman and Hall, London); *Alcoholic Fermentations*, by A. Harden (Longmans, Green and Co., London); also Acetic Acid, Acetone, Beer, Carbon Dioxide, Enzymes, Methane, Wine, and Yeasts.

**FERRATES** — See Iron Compounds.

**FERRIC SALTS** — See Iron Compounds.

**FERRICYANIDES** — See Cyanogen.

**FERRITE** — Solid solutions in which the alpha or the delta form (body centred modification) of iron is the solvent. (See Iron-Carbon system under Iron.)

**FERRITES** — See Iron Compounds.

**FERRO-ALLOYS** — See Iron.

**FERRO-CERIUM (Pyrophoric Alloys)** — See Iron, and Pyrophoric Alloys.

**" FERROCRETE "** — See Cement.

**FERROCYANIDES** — See Cyanogen.

**FERRO-MANGANESE** — See Manganese.

**" FERRO-PRUSSATE "** — Trade name for potassium ferrocyanide.

**FERRO-SILICON** — See Iron.

**FERROUS METALS** — See Iron.

**FERROUS SALTS** — See Iron Compounds.

**FERRUGINOUS** — Containing iron. Many natural mineral waters are ferruginous in character and act as tonics. (See Chalybeate Waters.)

**FERTILIZERS** are materials applied to assist or promote plant growth. As commonly defined, fertilizers include materials supplying the major elements nitrogen, potassium, and phosphorus, but since many other elements have been found to be essential to plant life, fertilizers may include a wide variety of materials, including the " minor elements," such as copper, boron, cobalt, manganese, etc. In so far as they supply plants with calcium and magnesium, liming materials may also be considered as fertilizers.

The important fertilizers may be classed as inorganic and organic. The former include ammonium sulphate, nitrate, and chloride, rock phosphates, superphosphate, basic slag, potash (potassium) salts, sodium nitrate (Chile nitre), lime, marl, dolomite, calcium nitrate, calcium sulphate (gypsum), sulphur, and others. The organic fertilizers include many plant and animal materials, such as stable manure, guano, slaughter-house refuse (tankage), dried blood, bonemeal, cottonseed meal, seaweed, fish meal, straw, and plant refuse (compost). Mixed fertilizers, containing several ingredients, are designed to supply the essential elements in approximately the proportions required by a specific crop: thus mixtures are available, for example, containing 5 per cent. of nitrogen, 10 per cent.  $P_2O_5$ , and 5 per cent.  $K_2O$ . Such a mixture is frequently designated as 5-10-5. These fertilizers usually contain both inorganic and organic materials, so that the ingredients may be available to the plants over a relatively long period of time.

The important nitrogen-containing fertilizers are salts of ammonia, such as the sulphate and nitrate. The former has the disadvantage of leaving an acid residue in the soil. Ammonium nitrate is exceptionally high in nitrogen content (approximately 50 per cent.). Ammonium fertilizers are produced as by-products of the destructive distillation of coal, or synthetically by fixation of atmospheric nitrogen. Sodium

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nitrate is widely used as a nitrogenous fertilizer. This is derived from natural sources; rich deposits are located in Chile. Guano, stable manure, dried blood, tankage, oil-seed cake, fish meal, and urea are all important organic fertilizers containing nitrogen. These are usually more slowly available to plants than the inorganic compounds, and thus exert their beneficial effects over longer periods of time.

The most important source of phosphorus-containing fertilizers is phosphate rock. Deposits are found in North Africa, France, United States (Florida and several western states), and on a number of islands of the Pacific. New Zealand deposits contain over 80 per cent. tricalcium phosphate, while the North African deposits average approximately 60 per cent. The rock phosphate is treated with acid for the production of fertilizers (see Phosphorus (Phosphates), and Superphosphate). Most plant and animal products contain small amounts of phosphorus, so that applications of these materials as fertilizers add to the supply of this element to plants.

There has been a marked activity in the development of phosphate fertilizer production in the United States in connection with the undertakings of the government in the Tennessee Valley Authority, and other phosphate deposits in Idaho and Montana are being explored.

Potassium is applied as fertilizers in the form of potassium chloride (muriate) or sulphate. Formerly most of the potassium used in fertilizers came from natural deposits in Germany; more recently natural brines have been used to a considerable extent (see Potassium). Wood ashes are rich in potassium, and are used in a limited way as fertilizers.

*References:* *Chemical Fertilizers*, by S. H. Collins (Baillière, Tindall and Cox, London); *Chemical Fertilizers*, by H. Cave (Sir Isaac Pitman and Sons, London); *Artificial Fertilizers*, by Parrish and Ogilvie (Ernest Benn, London); *Fixed Nitrogen*, by H. A. Curtis (Reinhold Publishing Corp., New York); *Commercial Fertilizers, Their Sources and Use*, by G. H. Collings (Blakiston Co., Philadelphia); *Fertilizers*, by F. E. Bear (John Wiley and Sons, New York); *Soils and Man* (Yearbook of Agriculture, 1938, U.S. Department of Agriculture, Washington, D.C.); *Ann. Rep. Prog. Appl. Chem.* (Society of Chemical Industry, London); Bones, Caliche, Coprolites, Cyanamide, Nitrogen, Nitrogen Fixation, "Nitrophoska," Phosphate Rock, Potassium, Soils, Slag, "Superam," Superphosphate of Lime, Urea, and Vegetation.

#### ESTIMATE OF WORLD FERTILIZER CONSUMPTION, 1936

Compiled from communication by A. N. Gray to First International Fertilizer Congress, Rome, 1938.

**Nitrogen (N):** 2,214,000 metric tons, amounting to 26 per cent. of the total fertilizer consumption, and distributed in 12,013,000 metric tons of commercial fertilizer.

**Phosphoric Acid ( $P_2O_5$ ):** 4,053,000 metric tons, amounting to 47 per cent. of the total fertilizer consumption, and distributed in 22,855,000 metric tons of commercial fertilizer.

**Potash** ( $K_2O$ ): 2,295,000 metric tons, amounting to 27 per cent. of the total fertilizer consumption, and distributed in 7,062,000 metric tons of commercial fertilizer.

# WORLD FERTILIZER PRODUCTION FOR THE YEARS 1939 AND 1944

Authority: *The Mineral Industry of the British Empire and Foreign Countries* (Imperial Institute, London).

Data arranged and rounded off by the Editor.

Nitrogen-containing Material, and Country					1939 Long Tons	1944 Long Tons
Sodium nitrate:						
Chile	..	..	..	..	1,420,000	975,000
France	..	..	..	..	100,000	10,000
Ammonium sulphate:						
Great Britain	..	..	..	..	550,000	840,000
France	..	..	..	..	300,000	90,000
Belgium	..	..	..	..	250,000	?
Italy	..	..	..	..	280,000	?
U.S.A. (coke ovens)	..	..	..	..	600,000	840,000
Canada	..	..	..	..	120,000	190,000
Japan	..	..	..	..	990,000	700,000
Manchuria	..	..	..	..	160,000	?
Ammonium phosphate:						
Italy	..	..	..	..	30,000	?
Canada	..	..	..	..	30,000	120,000
Ammonium nitrate:						
France	..	..	..	..	140,000 (?)	160,000
Italy	..	..	..	..	40,000	?
Calcium nitrate:						
Norway	..	..	..	..	340,000	440,000 (?)
Italy	..	..	..	..	190,000	?
France	..	..	..	..	120,000	130,000
Calcium cyanamide:						
Italy	..	..	..	..	210,000	?
France	..	..	..	..	50,000	5,000
Norway	..	..	..	..	30,000	50,000 (?)
Belgium	..	..	..	..	20,000	?
Canada	..	..	..	..	150,000	?
Japan	..	..	..	..	170,000	160,000
Chemical nitrogen (N-content):						
Germany	..	..	..	..	940,000	840,000
U.S.S.R.	..	..	..	..	140,000	?

## FERTILIZERS

Phosphorus-containing Material, and Country					Tribasic Phosphate of Lime ( $\text{Ca}_3(\text{PO}_4)_2$ )	
					1939 Long Tons	1944 Long Tons
Phosphate rock :						
France	..	..	..	..	30,000	60,000
Sweden	..	..	..	..	5,000	90,000
Belgium	..	..	..	..	15,000	60,000
Spain	..	..	..	..	5,000	10,000
U.S.S.R.					1,380,000	700,000
French Morocco					1,220,000	1,100,000
Tunis	..	..	..	..	980,000	320,000
Egypt	..	..	..	..	350,000	200,000
Algeria	..	..	..	..	310,000	140,000
U.S.A.					2,870,000	3,660,000
Nauru Island					800,000	?
Ocean Island					270,000	?
Christmas Island					150,000	?
Anguar Island					110,000	20,000
Japanese Islands (not Anguar Is.)					190,000	25,000
French Oceania					140,000	160,000
Ammonium phosphate :						
See same in preceding Nitrogen section.						
Superphosphate :						
Italy	..	..	..	..	1,580,000	25,000 (?)
France	..	..	..	..	1,170,000	5,000
Netherlands	..	..	..	..	560,000	?
Great Britain	..	..	..	..	450,000	860,000
Spain	..	..	..	..	410,000	310,000
Denmark	..	..	..	..	380,000	?
Portugal	..	..	..	..	210,000	340,000
Sweden	..	..	..	..	260,000	260,000
U.S.S.R.					1,570,000	1,000,000
U.S.A.					3,760,000	6,640,000
Japan					1,440,000	110,000

Potassium-containing Material, and Country	K <sub>2</sub> O Content	
	1939 Long Tons	1944 Long Tons
Potash minerals :		
Germany .. .. .	1,570,000	1,580,000
France .. .. .	600,000	460,000
Spain .. .. .	25,000	110,000
U.S.S.R. .. .. .	120,000 (?)	?
U.S.A. .. .. .	280,000	750,000
Palestine .. .. .	30,000	50,000

*Note :* See also Fertilizer Nitrogen under Nitrogen ; Phosphate Rock under Calcium (Phosphate) ; and Potash Minerals under Potassium.

**FIBRES** — The principal textile fibres are of vegetable or animal origin, or produced synthetically.

Vegetable fibres are plant cells, capable of withstanding fairly high heat, and not readily attacked by dilute alkalis to cause weakening. They are essentially composed of cellulose. Concentrated sodium hydroxide, however, forms alteration products, whereas sulphuric acid rapidly destroys the fibre, and concentrated nitric acid either forms nitrates or oxidizes the fibre. The principal vegetable fibres are cotton (see same), flax (see same), hemp (see same), ramie (see same), esparto (see same), sisal (see same), manila hemp (see same), and coconut fibre (see same).

Animal fibres are chiefly wool (see same) and silk (see same). These fibres are attacked by dilute alkalis and dissolved. With concentrated nitric acid a yellow coloured xanthoproteic acid is formed. Hairs are also animal fibres of importance.

#### WORLD'S PRODUCTION OF MAJOR CLOTHING FIBRES COMPARED TO WORLD'S POPULATION FOR SELECTED PERIODS

Authority : Food and Agricultural Organization of the United Nations,  
Washington, U.S.A., 1947

Data arranged by the Editor.

Annual Average in Period	World's Population	World's Production of Major Clothing Fibres in Thousands of Metric Tons and Percentages of Each				
		Total	Cotton	Wool	Silk	Rayon
1890	1,520,000,000	3,488	2,700 78·6	726 21·1	12 0·3	0 0·0
1909-13	1,790,000,000	5,534	4,662 84·3	834 15·0	29 0·5	9 0·2
1929-33	2,030,000,000	6,987	5,730 82·2	961 13·8	57 0·8	239 3·4
1939-43	2,170,000,000	8,301	6,039 72·8	1,062 12·8	45 0·5	1,155 13·9
1946	2,250,000,000	6,421	4,661 72·6	986 15·4	16 0·2	758 11·8

Most synthetic fibres are modified cellulose (see Silk Substitutes ; and " Film and Fibres Derived from Cellulose," by Levenstein (*J.S.C.I.*; 49, 77 T (1930)), although remarkable synthetic fibres of protein-like structure are now produced in large quantities for use in textiles, cordage, and brushes. (See Nylon, and " Orlon.")

*References* : *The Fundamentals of Fibre Structure*, by W. T. Astbury (Oxford University Press) ; *Physics and Chemistry of Cellulose Fibres*. by P. H. Hermans (Elsevier Publishing Co., New York and London) . *Flameproofing Textile Fabrics*, by R. W. Little (Reinhold Publishing Corp., New York) ; *Matthews' Textile Fibers*, by H. R. Mauersberger (John Wiley and Sons, New York) ; *Rubbers, Plastics, and Fibers*, by G. F. D'Alelio (John Wiley and Sons, New York).

**FIBRIN (Syntonin)** — A constituent of the blood which separates from it upon coagulation (clotting). It is of an albuminoid character, and its composition is approximately as shown :

	Per cent.
Carbon .. .. .	52.7
Hydrogen .. .. .	6.9
Nitrogen .. .. .	15.4
Oxygen .. .. .	23.5
Sulphur .. .. .	1.2
Phosphorus .. .. .	0.3
	<hr/> 100.0

It has been conjectured that the clotting of blood is brought about by an enzyme in the blood called thrombose (thrombin). This fibrinolytic agent (also named thrombolysin) is stated to exhibit its maximum activity at 37° C. in neutral solution ; to be precipitable by alcohol, ammonium sulphate, and zinc chloride ; and to become inactivated at 46° to 48° C.

**FIBROLITE** — A trimorphous mineral of similar composition to andalusite.

**" FIBROX "** — A variety of " Siloxican," being a soft, elastic, fibrous material of pale greyish-blue colour. (See " Siloxican.")

**FILM COEFFICIENT** — See Heat Transfer.

**" FILTER-CEL "** — A proprietary infusorial filtering earth agent.

**FILTRATION** — The separation of suspended solids from a liquid by passing it through a porous medium. Filters are of three main types : gravity filters, suction or vacuum filters, and pressure filters. They are further classified as intermittent or continuous.

Laboratory filters include the familiar glass funnel with either plain or pleated filter paper, the Büchner funnel, the Gooch crucible, sintered glass and porcelain filters, and micro-filters of various kinds. The internal angle of an ordinary filter funnel should be exactly 60 degrees, otherwise the folded paper will not fit closely and filtration will be slower. It has been stated that the rate of flow of liquid through a

filter paper is appreciably affected by the manner of folding; it is slightly faster if the folds are produced by gentle pressing rather than by sliding the finger and thumb along them.

The design of industrial filters aims firstly at providing a large area of filtering surface in a small volume, and secondly, at securing either continuous operation or the shortest possible interruption between runs. The simplest type is the gravity filter, which usually consists of a shallow vessel having a perforated bottom covered with a filter medium such as cloth. In large gravity filters a bed of sand may be used, supported on broken stone.

Any gravity filter becomes a vacuum filter if suction is applied below the filter medium, but vacuum filters are usually provided with extended surfaces. A simple form has a number of "filter leaves" suspended in an open tank containing the liquid to be filtered. Each leaf consists of a cloth bag stretched over a U-shaped frame of perforated pipe. Suction applied to the pipe draws clear liquid through the bag, solids being deposited on the outside.

Vacuum filtration has the drawback that the driving force which can be applied is limited to something less than atmospheric pressure, and filter rates are therefore comparatively low. It has the advantage that since the solids accumulate on the outside of the filter unit they can be continuously scraped off, and the principal industrial use of vacuum filters is for continuous filtration. One of the first continuous vacuum filters was the Oliver, which consists of a rotating drum covered with filter cloth and partly immersed in a tank of liquid. The inside of the drum is divided into sectors, and an arrangement of ports provides that those sectors immersed in the liquid are under vacuum, but that after a sector has emerged from the liquid some compressed air is admitted, thus loosening the filter cake, which is then detached by a fixed scraper. Another machine, the American filter, has a series of revolving filter discs on a hollow shaft in place of a drum.

Intermittent pressure filters include the filter press, perhaps the most widely used of all industrial filters. One form, the plate-and-frame press, has a number of grooved plates covered on either side with filter cloth and separated by frames or spacers, the whole assembly being carried between horizontal bars and closed by a powerful screw. The liquid to be filtered is pumped into the spaces between the plates, where the solids accumulate. Clear liquid passes through the filter cloths and via the grooves to an outlet pipe projecting from each plate. When the spaces are filled with solids the screw is relaxed, the plates and frames disassembled, and the solid filter cakes removed.

A second type of intermittent pressure filter is the Sweetland, which resembles in principle the simple vacuum leaf filter already described, but the leaves are enclosed in a steel shell into which the liquid to be filtered is pumped under pressure. A particular feature of these filters is the arrangement for quick opening and discharge of the cake.

Among special filters there is the Hele-Shaw streamline filter, composed of a pack of flat paper rings threaded over a perforated tube and compressed together. The pack is enclosed in a pressure vessel

receiving the liquid to be filtered. Clear liquid passes between the paper rings and into the perforated tube while solids are retained on the outside of the pack. These filters can remove extremely fine and even colloidal solids. Somewhat similar is the Metafilter, an edge filter having a pack of specially shaped metal plates which is precoated with a filter aid before use.

The theory of filtration has been quite fully investigated. Its principal value is in predicting plant scale filtration rates from laboratory tests.

*References:* Standard works listed under Chemical Engineering; *Theory and Practice of Filtration*, by G. D. Dickey and C. L. Bryden (Reinhold Publishing Corp., New York).

**"FILTROL"** — A decolorizing material, consisting of silica and about 7 per cent. of aluminium silicate, ground to pass a 200-mesh sieve, and stated to have three or more times the efficiency of standard fuller's earth.

**FIR-SEED OIL**, from the seeds of *Pinus abies* (L.) and allied species; used in making paints and varnishes, and reported to have a sp. gr. of 0.9295 at 15° C., solidifying-point of -26° C., sap. v. 191.8, i.v. (Hanus) 154, and to contain 91.6 per cent. non-volatile fatty acids, composed of 0.7 per cent. palmitic acid and 99.3 per cent. unsaturated acids (oleic, linolic, and linolenic). Oil of this name must, however, vary considerably in properties according to its source. Seeds from *Pinus sylvestris* (L.) yield an oil of sp. gr. 0.9307, solidifying at -30° C., sap. v. 190.7, i.v. (Hanus) 159.2, containing 9.7 per cent. liquid acids (oleic, linolic, and linolenic), together with 3 per cent. solid fatty acids (palmitic and stearic).

**FIRE HAZARDS** — See Hazardous Chemicals.

**FIRE-CLAY** — See Clays, Porcelain, and Refractories.

**FIRE-DAMP** — An explosive gas naturally produced in coal-mines, and chiefly composed of methane (marsh gas, CH<sub>4</sub>) admixed with air, nitrogen, and some carbon dioxide. The explosive limits of methane-air mixtures are 5.3 to 13.9 volume per cent. of methane.

**FIRE-PROOFING** — Some of the chemicals used in fire-proofing are employed because they fuse below the ignition point of the fabric, forming a non-inflammable layer on the surface; others, because at temperatures below the ignition point they decompose and evolve gases incapable of combustion, such as steam, carbon dioxide, and ammonia; a third class because they absorb heat by endothermic changes, including volatilization.

Ammonium salts are of some value for the fire-proofing of wood, the phosphate being probably the best, as on heating it gives off ammonia which is incombustible and leaves phosphoric acid, which melts and covers the fibres of the wood. Borax is not so good, but more economical. Among other salts claimed to be of use are potassium silicate, alum and borax in mixed solution, and the chlorides of calcium, zinc, and mercury. A paint known as "Calcimine," has been found

satisfactory for inside purposes, whilst for outside applications a coating of zinc borate and chrome green ground in linseed oil exhibits good fire-resisting properties.

A fire-proofing mixture for wood and thatch, as prepared from a Home Office formula, is made by dissolving 28 lbs. ammonium sulphate, 14 lbs. ammonium carbonate, 7 lbs. lump borax, 7 lbs. boracic acid, and 14 lbs. lump alum in 500 lbs. (50 gallons) water.

For use in connection with fabrics, the effects of the chemicals and associated treatment upon the fabrics have first to be considered, some having a tendering effect and others causing deterioration of quality or encouraging the growth of micro-organisms. It must also be borne in mind that after treatment they will probably be exposed to rain or water, ruling out of use many soluble agents (*Ind. Chem.*, 9, 223 (1933)). (See "Erifon.")

**FIREWORKS (Pyrotechny)** are luminous devices made from combustible or explosive chemicals, largely dependent upon the use of gunpowder, metallic filings being introduced to produce scintillation, and many chemicals being used in association to produce colouring and other effects. (See Flame Coloration.)

**FIRST RUNNINGS**, resulting from tar distillation, is the fraction up to 105° to 110° C., containing water, ammonia, and some light oil.

**FISCHER-TROPSCH PROCESS** — See Fuel (Liquid).

**FISH GLUE** — See Glue, and Isinglass.

**FISH MEAL** — See Feeding Stuffs.

**FISH OILS** are of the non-drying class, and usually have an offensive odour, which, however, is largely removed in the chemical changes brought about by their hydrogenation. (See Hydrogen (Hydrogenation).)

The commercial fish oils are in the main devoid of the liver oils (the livers, when of value, being first of all removed), and are obtained from all parts of the common fish, such as herring, sardine, salmon, sprat, etc., by boiling the fish in a tank with a perforated grid to support the fish, during which operation the oil rises to the surface and is then removed, being a high-grade oil of pale colour. The dried fish residue is subsequently extracted with benzene, by which a dark oil is obtained which requires refining. Cod-fish contains only 1·8 per cent. oil and ling 2·2 per cent., so that they are not rich enough in oil to be treated by this process. Blubber oils are obtained from the whale, seal, and turtle by boiling the blubber. Fish oils upon standing in the cold are subject to the deposition of stearin.

**Cod-Liver Oil** is obtained by steam-heating in jacketed pans or blowing the steam direct into the livers of various species of *Gadus*, and especially from the torsk (*Brosimus brosme*). Large quantities are imported from Norway and Newfoundland, a proportion of the stearin contained therein being first of all removed by cooling; in the case of Norwegian oil, the amount removed is from 3 to 5 per cent. The oil has a sp. gr. of from 0·92 to 0·93, sap. v. 187 to 197·5, i.v. 150 to 181, 14\*

ref. ind. 1·479 to 1·483, acid v. about 2·5, and solidifies at 0° to -10° C. It is stated to contain (in addition to palmitic, myristic, and stearic acids) zoomaric acid ( $C_{16}H_{30}O_2$ ), which is said to be a constituent of the oils and fats of most marine animals.

The oil is largely used as a nutritive food, also in medicine and for leather-dressing. Its therapeutic value would appear to depend upon its ready digestibility, absorbability, and its vitaminic character, which latter is liable to depreciate by any oxidative change to which it may be exposed. (See Cholesterol, and Vitamins.)

**Dugong Oil (Manatee Oil)**, from the blubber of the sea cow (*Halicore indicus*) ; sp. gr. 0·924 at 15° C., sap. v. 204·7, i.v. 52·5 (Hübl), acid v. 0·3, opt. rot. at 40° C. -0·12° ; used to replace cod and whale oils and for burning (in India.)

**Halibut-Liver Oil** has sp. gr. 0·927 at 25° C., sap. v. 179-193, i. v. 118-126, contains vitamin A. (See Emmett and Bird in *Ind. Eng. Chem.*, 24, 1072 (1932) ; Haines and Drummond in *British Medical Journal*, 1933, 559.)

**Herring Oil** is yellowish-red, with a sp. gr. about 0·92, sap. v. 180 to 194, i.v. 120 to 142, ref. ind. 1·480 at 15° C., acid v. 6·53. It is soluble in carbon disulphide, benzene, and ether, and contains about 19 per cent. saturated acids, including palmitic and myristic acids, the bulk consisting of acids of the oleic series. It is used in making printing-ink, soap, leather-dressing, and the steel industry, while the meal is a useful food for poultry and animals. (See Feeding Stuffs.)

**Menhaden Oil** — A yellowish-red oil extracted from the menhaden or moss-bunker fish, having a solidifying-point of -4° C., sp. gr. 0·927 to 0·933, sap. v. of 191 to 196, and i.v. 142 to 180. It is soluble in ether, naphtha, carbon disulphide, and benzol, and is used in rope and leather-dressing, paint and varnish making (in combination with or substitution for linseed oil), etc.

**Pilchard Oil** — Resembles herring oil in general respects, and is yielded by pressure from the pickled fish (*Clupea pilchardus*, a member of the herring family) to extent of from  $\frac{3}{4}$  to 1 gallon per cwt. It is of a pale yellowish-brown colour, with little objectionable odour, and deposits stearin on long standing ; contains 8·15 to 9·32 per cent. free fatty acids calculated as oleic acid, is of sp. gr. 0·9328 to 0·9313, sap. v. 186 to 189·6, i.v. (Wijs) 170·4 to 172·7, ref. ind. at 40° C. 1·4751 to 1·47425, and makes a good pale, amber-coloured potash soft soap.

**Porpoise Oil** is extracted from the brown porpoise, and is of pale yellow colour, sp. gr. about 0·926, sap. v. 195 to 256, and i.v. (varying with the part of the body yielding same) from 88 to 119. It is soluble in ether, chloroform, carbon disulphide, and benzol, and used in making lubricants, soaps, leather-dressing, etc. The quality from the jaw of the porpoise is used as a lubricant for watches. According to C. M. Tucker, the oil from the head of *Tursiops truncatus* showed sp. gr. 0·9241 ; ref. ind. at 20·5° C. 1·4519 ; sap. v. 293 ; i.v. (Hanus) 28·3 ; Reichert-Meissl v. 139 ; acid v. 2·88 ; and the approximate analysis as : dodecyl alcohol 18·7, glycerol 18·5, isovaleric acid 62·6, palmitic acid 6·1, oleic acid 3·5 per cent.

**Salmon Oil** — A by-product of the canning trade, being a yellowish liquid of sp. gr. 0.9258, sap. v. 182 to 188, i.v. 161 to 190; soluble in alcohol, ether, etc., and used in soap-making and leather-dressing, and in paints and exterior wood stains.

**Sardine Oil** is of a yellow colour, of sp. gr. about 0.93, sap. v. about 189, i.v. 158 to 190, and ref. ind. 1.48. It is soluble in alcohol, naphtha, etc., and is used in soap-making and as a lubricant. A characteristic fatty acid of the fish-oil group is named *clupanodonic acid* ( $C_{22}H_{34}O_2$ ), which notably occurs in the mixed fatty acids obtained from Japanese sardine oil, herring and whale oils, etc.,. It is a pale yellow liquid of fishy odour, which does not solidify at  $-50^\circ$ , and readily oxidizes on exposure to the air to a varnish-like mass.

**Seal Oil**, is white or straw-coloured, of sp. gr. 0.924 to 0.926, sap. v. of 189 to 196, i.v. 127 to 193, and ref. ind. 1.474. It closely resembles whale oil (*Balaena* genus); is soluble in benzene, chloroform, ether, and carbon disulphide; and is used in soap-making.

**Sea-Wolf Liver Oil** (from *Anarrhichas lupus* L.) is of golden-brown colour, curious odour, and contains about 92.2 to 92.4 per cent. fatty acids; sap. v. 182 to 185, and i.v. (Wijs) 118 to 131; used in Russia for mixing with codfish liver oil in the tanning industry.

**Shark-Liver Oil** (*Squalus acanthias*) — This oil closely resembles cod-liver oil, having a sp. gr. at  $15^\circ$  C. of 0.9248, sap. v. 188, i.v. 154 to 172, and ref. ind. at  $25^\circ$  C. of 1.4761. It can be hydrogenated to a solid state; is yellow to reddish-brown in colour, and in addition to its pharmaceutical applications can be used in soap-making, in paint manufacture, and for currying leather. It is also used as an adulterant of cod-liver oil. The unsaponifiable constituents of shark- and ray-liver oils are stated to consist chiefly of higher alcohols (butyl, chimyl, and selachyl alcohols).

**Sperm (Whale) Oil** — The oils from the head and the blubber of the genera *Physeter* and *Hyperoodon* (or sperm and bottle-nosed whales) differ in composition and are characterized by almost complete absence of glycerides, esters of the higher aliphatic alcohols taking their place. According to Hilditch, they exhibit the following analytical features: Head oil: sp. gr. 0.878 to 0.880; ref. ind. 1.459 at  $25^\circ$  C.; sap. v. 140 to 144; i.v. 60 to 76. Body oil: sp. gr. 0.871 to 0.877; ref. ind. 1.462; sap. v. 122 to 130; i.v. 80 to 93. Sperm oil is used, among other applications, as a bath for immersion of steel in hardening it for cutting purposes. (See Whale Oils.)

**Tope-Liver Oil** (*Galeus galeus*) has values very nearly like those of cod-liver oil, namely, sp. gr. 0.9249, i.v. (Wijs) 152.2, sap. v. 185.1, ref. ind. at  $15^\circ$  C. 1.4803. It is of pale colour, rather strong odour, is used for leather-dressing, and is equal to cod-liver oil as a source of the fat-soluble vitamins.

**Tuna Oil (Tunny-Fish Oil)** is pale yellow to red-brown in colour, and is expressed from the livers of *Thynnus vulgaris*; i.v. about 156; soluble in alcohol, ether, etc., and used in paint-making, etc.

**Whale Oil (Blubber Oil)** is obtained chiefly from the blubber of *Balaena*

*mysticetus* and many other species. There are a number of grades, varying in colour from almost water-white to yellowish-brown; it solidifies at about 2° C.; sp. gr. varying from 0.908 to 0.925, sap. v. 188 to 196, and i.v. 114 to 126. It is soluble in alcohol and ether, has a strong fishy odour, and is used in soap-making, for lubricating, tempering steel, and as a leather dressing. By hydrogenation it is converted into a hard, white, inodorous fat, constituting a good substitute for tallow. A tetradecylenic (tetradecenoic) acid ( $C_{14}H_{26}O_2$ ) has been isolated from sperm oil.

**FISH PRODUCTS** — See Feeding Stuffs, Fish Oils, and Oils.

**FISSION** — The splitting of certain atoms by absorption of slow-moving neutrons into two atoms of more or less equal weight plus more neutrons, thus causing a chain reaction. Such atoms are uranium 235, and plutonium 239. (See Nuclear Chemistry.)

**FIXED OILS** — See Oils.

**FIXED POINTS** — See Heat (Temperatures).

**FLAME COLORATION** — Many chemical compounds communicate distinct coloration to an otherwise colourless or nearly colourless flame, such as that of the blow-pipe or Bunsen burner. (See Boron, and Light (Spectroscope).)

Potassium salts give a lilac colour to the flame.

Sodium     "     "     yellow     "     "

Calcium    "     "     brick-red   "     "

Barium     "     "     green       "     "

Strontium   "     "     red         "     "

Copper     "     "     green       "     "

Lithium    "     "     brilliant crimson colour to the flame.

Lead, arsenic, and antimony compounds give a bluish-white colour to the flame.

**FLAME-PROOFING** — See Flame-proofing, and Nitrogen Compounds (Ammonium Sulphamate).

**FLAME TEMPERATURES** — Some flame temperatures have been determined as follows: water gas, Bunsen burner and other gas flames ranging from 1,860° to 1,870° C.; hydrogen gas, 1,900° C.; oxy-hydrogen, 2,800° C.; oxyacetylene, 3,300° C.

*References:* Bone, Newitt, and Townend on *Gaseous Combustion at High Pressures* (Longmans, Green and Co., London); Bone and Townend on *Flame and Combustion in Gases* (Longmans, Green and Co., London).

**FLASH-POINT** is the temperature at which an oil or other combustible liquid gives off vapour, which will then fire or explode if mixed with air and exposed momentarily to a naked light.

"That mixture containing the minimum amount of fuel gas or vapour capable of producing an explosion on ignition is known as the lower ignition mixture, and that containing the maximum amount of fuel which will still explode on ignition as the upper explosive mixture. In dealing with liquids, the lowest temperature at which the liquid in contact with air will give the explosive mixture with the minimum

amount of fuel is known as the lower flash-point, and the lowest temperature at which the liquid will give an explosive mixture with the maximum amount of fuel is known as the upper flash-point."

The flash-point is an empirical constant depending to some extent upon the particular apparatus used for determining it. Ormandy and Craven find that there is an approximately linear relation between the flash-point and boiling-points measured on the absolute scale, and that the ratio is close to 0.734. The difference between the results obtained, using the various kinds of apparatus, lies, to some extent, in the variations in the ratio of the vapour space above the liquid to the volume of the latter, the vapour pressure having an important influence on the flash-points. At the flash-point in air, all hydrocarbons have approximately identical vapour tensions. The flash-point is raised by the increase of pressure, while it is lowered when oxygen is substituted for air. (See Ignition.)

The U.S. Interstate Commerce Commission regulation requires a *red* shipping label to be attached to containers holding liquids with flash-points at or below 80° F. or 26.5° C.

#### FLASH-POINTS OF VARIOUS ORGANIC LIQUIDS

Data assembled by the Editor.

Key to authorities cited in parentheses:

F—Florentin (1928).

M—Mack *et al.* (1923).

R—Richardson and Sutton (1928).

S—Schwartz (1918).

U—Underwriters' Laboratories Inc. (1929).

Solvent	Flash-Point, ° C.
Diethyl ether .. ..	−40 (R) ; −20 (S) ; −45 (U)
Gasoline .. ..	−43 to −18 (U)
V. M. & P. naphtha ..	−40 to −7
Carbon disulphide ..	−25 (M) ; −20 (S) ; −30 (U)
Acetone .. ..	−20 (F) ; −20 (R) ; −16 (U)
Petroleum ether ..	−20 (S)
Hexane .. ..	−18 (M)
Pentane .. ..	−18
Benzol .. ..	−9 (M) ; −15 (S)
Benzene, 90% ..	−12 (R) ; −20 (U)
Ethyl alcohol, absolute	−12 (F) ; +9 (M) ; +13 (R)
Ethyl alcohol, 95% ..	+11 (F) ; +14 (S)
Ethyl alcohol, 45% ..	+20 (S)
Methyl formate ..	−12 (F)
Methyl acetate ..	−11 (F) ; −15 (M) ; −10 (U)
Benzine .. ..	−8 (F)
Methyl alcohol ..	−7 (F) ; +6 (M) ; +12 (R) ; 0 (S) ; +11 (U)
Ethyl chloride ..	−7
Ethylene oxide ..	−7

## FLASH-POINT — FLASKS

Solvent	Flash-Point, ° C.
Ethyl acetate ..	-3 (F) ; -5 (M) ; +3 (R) ; -2 (U)
Isopropyl acetate ..	+5 (M) ; +5 (R)
Toluene ..	+7 (M) , +8 (R) ; +7 (S) ; +9 (U)
Isopropyl alcohol ..	+15 (M) , +12 (R) ; 16 (U)
Ethylene dichloride ..	+14
<i>n</i> -Propyl acetate ..	+15 (M)
Ethyl benzene ..	+15 (M)
Octane ..	+17 (M)
<i>n</i> -Propyl alcohol ..	+21 (F) ; +23 (M)
<i>n</i> -Butyl acetate ..	+22 (R) ; +28 (U)
Isobutyl acetate ..	+22 (F)
Xylol ..	+30 (S) ; +30 (U)
<i>n</i> -Butyl propionate ..	+32 (R)
Amyl acetate ..	+32 (R) ; +25 (U)
Amyl acetate, commcl.	+32 (F)
Butyl alcohol ..	+40 (F) ; +35.5 (M) ; -1.29 (R) ; +38 (U)
Isobutyl alcohol ..	+28 (M) ; +31 (U)
Butyl alcohol, ferm. ..	+32.5 (F)
Amyl alcohol ..	+46 (F) ; +33 (R) ; +38 (U)
Isoamyl alcohol ..	+40 (M) ; +46 (U)
Fusel oil ..	+46 to +54 (S)
Monochlorobenzene ..	+27.5 (S)
Turpentine ..	+38 (F) ; +35 (S)
White spirit, boiling range 150°-200° C. ..	+39 (F)
Ethyl lactate ..	+43 (R)
Nitrobenzene ..	+90 (S)

**FLASKS** are glass or metallic vessels of varying shapes for holding chiefly liquids, consisting generally of a body part with flattened bottom, having a neck which can be easily grasped by the hand or held by a clamp, and closed with a stopper when required. When made of glass the quality should permit the contents to be heated. (See Aspirator, and Gas Generators.)

**Dewar Flasks** — See Vacuum.

**Distillation Flasks** are of the round bottom type with a side outlet at a specified position in the neck. A thermometer is placed so that the top of its bulb is opposite the lower part of the side outlet of the flask.

**Erlenmeyer Flasks** are of conical type, having flat bottoms of diameter equal to from one-half to three-fourths of the height, and with side surface tapering smoothly from the base to the bottom of the neck, which is short, narrow, and straight-sided. They have the advantage of being more easily washed out than round flasks.

**Kjeldahl Flasks** are of the round bottom, long neck type for first digesting liquids, and then distilling. The long neck functions as a partial condenser (see Kjeldahl's Process).

**FLAVIN** — See Quercetin.

**FLAVONE** ( $C_{15}H_{10}O_2$ ) — The parent of many yellow and orange plant pigments, which occur, not in plastids (see Chlorophyll), but dissolved in the cell-sap. They often occur as glycosides, and fall into two classes, *flavones* and *flavonols*, the latter being hydroxy derivatives of the former. The flavones, anthocyanidins, and pyrocatechol tannins are all derived from the same carbon frame-work, that of 2-phenyl-benzopyrone. For instance, quercetin, a flavone, can be reduced to cyanidin, an anthocyanidin, by a suitable process. (See Galanga, Morin, Plant Colouring Matters, and Quercetin.)

**FLAX** (*Linum usitatissimum*) is a plant (genus Linaceæ) extensively grown in Ireland, Belgium, Germany, France, Russia, and other countries for the sake of the fibre (which is the raw material of linen), the linseed oil which is extracted from it by pressure, and the residual cake which is used for cattle food. It contains from 32.77 to 38.42 per cent. of fat, including about 1.65 per cent. wax, and from 3.33 to 5.29 per cent. nitrogen. Flax wax is for the most part found present in the fibre and cortical tissues, the air-dried cortex sometimes containing as much as 10 per cent. Various varieties of the wax have a sap. v. of 77.5 to 83.7, i.v. 21.6 to 28.8, acid v. 17.5 to 23.8, m.p. 67.3 to 69.8, and sp. gr. 0.963 to 0.985, the water-retted kinds being richer in wax than the dew-retted. It is stated to contain ceryl alcohol and cerotic acid, takes a high polish, and can be used as a substitute for beeswax for some applications. New Zealand flax is an important fibre derived from a different plant, namely, *Phormium tenax*, of the order Liliaceæ.

The pectin content of various flaxes appears to range from 4.46 to 7.02 per cent., while that of flax fibre bundle when separated from cortical tissues is under 2 per cent.

The retting of flax is a process for preparing it by soaking and maceration, involving in large measure the action of associated bacteria, and is conducted in order to remove the boon or woody part and associated gummy and resinous substances.

The waste liquor obtained as the result of retting flax contains large proportions of organic matters, and requires to be purified either by chemical precipitation with lime and aluminium sulphate, biological treatment, or irrigation overland, before discharge into streams.

Fibres of flax and ramie can be distinguished from those of hemp, after isolation in warm water, by viewing them while drying in a warm room, as they always twist in a clockwise fashion, while hemp and jute rotate in an opposite direction. (See Lignin, Linseed Oil, Pectins, and Waxes (Flax).)

“**FLAXEDIL**” — A stable, water-soluble compound, namely, tri-(diethylaminoethoxy)-benzene triethyliodide, used as a synthetic substitute for *d*-tubocurarine chloride in producing muscular relaxation prior to surgical operation. (See W. W. Mushin, *et al.*, (*Lancet*, **256**, 726 (1949)); W. D. M. Paton (*J. Pharm. Pharmacol.* **5**, 273 (1949)); Decamethonium Iodide, and *d*-Tubocurarine Chloride.)

**FLEA SEED** — See Psyllium Seed.

**"FLEXSTEL"** — Patented expansible and flexible joints in steel and other metals capable of withstanding fluctuating and intermittent pressures.

**FLINT** — A variety of quartz. (See Silicon (Silica).)

**FLOCCULATION** — See Agglomerating Agents.

**FLORESCENCE** — A term used in respect of the crystallization of soluble salts on the surfaces of building materials. These may be washed off by the application of dilute acids, say dilute hydrochloric acid, or vinegar, followed by washing with water.

**FLORIDIN** — A variety of fuller's earth found in Florida (U.S.A.), used in granulated form (16- to 30-mesh), after ignition at 900° F., as a decolorizing agent in wax-refining, etc., and admitting of regeneration by furnacing.

**FLORIDOSE** — An aldohexose occurring in red sea-weed of the *Florideæ*, etc.

**FLOTATION OILS AND PROCESS** — See Ores and their Treatment.

**FLOW SHEET (Flow Diagram)** — A diagrammatic drawing illustrating the flow of materials through the various stages of a manufacturing process. It generally shows the quantities and compositions of all materials entering and leaving each stage of the process in unit time, and may also give the heat and power requirements. One of the first steps in the design of a chemical plant is to prepare an overall flow sheet, followed by detailed flow sheets for every section of the plant.

*References:* *Chemical Engineering Flowsheets*, a collection of typical examples published by *Chemical Engineering* (New York).

**FLUELLITE** ( $\text{AlFe}_3\text{H}_2\text{O}$ ) — A native fluoride of aluminium (crystal system No. 4, and sp. gr. 2.17).

**FLUID DYNAMICS** — The study of liquids and gases in motion. The dynamical properties of fluids are important to chemical engineers, more especially the property of forming laminar films at phase boundaries. When a fluid is flowing fairly rapidly through a pipe, the main stream is filled with turbulent eddies; but next to the pipe wall there is a thin film of fluid that is retarded by friction and creeps straight forward without turbulence, in laminar or streamline flow. If the fluid is to be warmed by heating the pipe, the heat must pass through this laminar film. It can only do so by conduction, since the motion of the fluid is parallel to the pipe wall and not towards or away from it. Once the heat has penetrated the film, it is quickly carried by eddy motion throughout the turbulent region. Since the thermal conductivity of most fluids is low, the laminar film constitutes the principal resistance to heat transfer from pipe wall to fluid.

When a solid substance is dissolving in a liquid that is briskly agitated, a laminar film of liquid adheres to the surface of the solid although the main bulk is in a state of turbulence. The molecules of solute must diffuse through this film before reaching the turbulent region, and once again the film constitutes the principal resistance to process.

In fluids that are moving past a solid boundary with sufficient velocity to maintain turbulence, the thickness of the boundary film is inversely proportional to the 0.8th power of the velocity; hence in this region, rates of heat and mass transfer vary directly as the 0.8th power of the fluid velocity. As the velocity is reduced, however, an ill-defined critical velocity is reached below which all turbulence in the fluid ceases and the motion is laminar throughout. Below this velocity, heat and mass transfer rates are exceedingly low. The critical velocity is a function of the density and viscosity of the fluid, and of the shape and size of the solid boundary. For the common case of fluids flowing through straight pipes which they completely fill, the critical velocity is given by the equation:  $\frac{\rho V d}{\mu} = 2,100$ , where  $\rho$  and  $\mu$  are respectively the density and viscosity of the fluid,  $d$  is the internal diameter of the pipe, and  $V$  the fluid velocity, all expressed in consistent units. The dimensionless group on the left of this equation is known as the Reynolds Number, often denoted by the symbol  $Re$ ; it is of fundamental importance in fluid dynamics.

The energy lost in fluid friction is partly absorbed by viscous shear in the laminar film, and partly by mutual interference of eddies in the turbulent region; the two components are termed respectively “skin friction” and “eddy loss.” The loss of head caused by fluid friction in pipes is given by the Darcy or Fanning equation:

$$\Delta h = \frac{2f l V^2}{g d}$$

where  $\Delta h$  = loss of head (in feet or cm. of fluid flowing),  $l$  = length of pipe,  $d$  = diameter of pipe,  $V$  = fluid velocity,  $g$  = acceleration of gravity, all in consistent units.  $f$  is a “friction factor” which depends upon the Reynolds Number. Below the critical velocity,  $f = \frac{16}{Re}$ ; above the critical velocity, in the region of turbulent flow,  $f$  is approximated by the Genereaux equation:

$$f = 0.04(Re)^{-0.16}$$

$f$  can be determined more accurately from the Reynolds-Stanton curve, which is a plot of  $f$  versus Reynolds Number, and is valid for all fluids, liquid or gaseous. It is found in almost all textbooks on fluid dynamics. The value of  $f$  varies somewhat according to the internal roughness of the pipe.

*References:* Standard works listed under Chemical Engineering.

**FLUOBORATES** — Salts of fluoboric acid  $\text{HBF}_4$ , which is formed by the reaction of  $\text{HF}$  and  $\text{BF}_3$ .

**FLUOR (Fluorspar, Fluorite)** — See Fluorine.

**FLUORAPATITE** — A mineral of composition  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ .

“**FLUOREMETIC**” — A soluble double fluoride of antimony and sodium being a clear white crystalline salt largely used in the textile trade.

**FLUORENE (Diphenylenemethane)** ( $\text{C}_6\text{H}_4\text{.CH}_2\text{.C}_6\text{H}_4$ ) is contained in

coal tar and can be obtained by passing diphenylmethane through red-hot tubes. It is a white crystalline substance exhibiting a violet fluorescence, of m.p.  $116^\circ\text{C}$ . and b.p.  $295^\circ\text{C}$ .

**FLUORESCEIN (Resorcinphthalein)** ( $\text{C}_{20}\text{H}_{12}\text{O}_5\text{.H}_2\text{O}$ ) is a dark red, crystalline powder, soluble in alcohol to a yellow-red colour, and in alkalis to a red colour, showing a fine green fluorescence. It is easily reduced to the phthaline "fluorescin," and by bromination gives the potassium salt known as the dye eosin. These substances are extensively used in the dyeing industries. (See Eosin.)

**FLUORESCENCE** — When a substance is exposed to high energy radiation (ultra-violet) the atoms or molecules absorb energy and become activated (see Light (Photochemical Aspects)). If the energy is not removed by collision or reaction, after about  $10^{-7}$  second the substance emits *fluorescent energy* with a frequency which is characteristic for each substance. In general, the emitted radiation has a lower frequency than the absorbed radiation. Fluorescence differs from phosphorescence in that when the activating energy is shut off fluorescence stops while phosphorescence lingers on for a while.

Alcohol solutions of anthracene, eosin, or esculine show fluorescence when exposed to white light. Water solutions of fluorescein, quinine sulphate, resorcin blue, or rhodamin also fluoresce when exposed to white light. Vapour of iodine, mercury, oxygen, potassium, rubidium, or sodium when properly excited by absorption of radiation gives off its own characteristic fluorescence; and, similarly, the minerals and gems known as agate, alunite, amethyst, apatite, borax, gypsum, pearl, ruby, sapphire, and zircon. (See "Fluorescence of Rubber and of Compounding Ingredients," by V. N. Morris (*Ind. Eng. Chem.*, **26**, 107 (1934)); "Fluorescence Analysis in Ultra-Violet Light," by Julius Grant (*Ind. Chem.*, **14**, 277 (1938)); *Fluorescence Analysis in Ultra-Violet Light*, by J. A. Radley and J. Grant (D. Van Nostrand Co., New York); *Fluorescence for Rapid Testing* (Hanovia, Ltd., of Slough); *Fluorescence and Phosphorescence*, by Peter Pringsheim (Interscience Publishers, New York); and Ultra-Violet Light.)

**FLUORINE (F) and its Compounds** — Atomic weight 19.00. See Elements for other data. Fluorine is found in nature combined with calcium in the mineral *fluorspar* or *fluorite* ( $\text{CaF}_2$ ), also known as *Derbyshire spar*, of crystal system No. 1, and sp. gr. 3.15 to 3.20. It is quarried in large quantities at Weardale and Alston, while workable deposits occur near Ottoshoop, Zeerust, South Africa. In the U.S.A., Kentucky and Illinois are the producing states. Fluorine is also a constituent of *cryolite* ( $\text{Na}_3\text{AlF}_6$ ), a double fluoride of sodium and aluminium found in Greenland, and some other minerals, for example, in varying proportions in apatite and phosphate rocks, and present in small quantities in bones and the enamel of teeth. (See "Removal of Fluorides from Drinking Water," by R. H. McKee and W. S. Johnston (*Ind. Eng. Chem.*, **26**, 849 (1934)); and "Defluorite".)

Fluorspar occurs in blue and green forms, and sometimes consists of 99.5 per cent. calcium fluoride. It is used for fluxing purposes in metallurgical furnace processes, and in the glass and enamel industries.

Fluorine can be obtained in quantity by the electrolysis of fused potassium hydrogen fluoride ( $\text{KHF}_2$ ), one electrode being of graphite, the other consisting of the copper container, the evolved gas being purified by passage through copper tubes filled with sodium fluoride in order to remove the hydrogen fluoride. It can also be prepared by the electrolysis of fused acid fluorides, using carbon-free iron or nickel anodes, and allowing the nickel or copper-containing vessel to act as cathode. By another process it can be made by the electrolysis of anhydrous hydrofluoric acid at  $-23^\circ\text{C}$ . It is, at ordinary temperatures, a pale yellowish gas of very active chemical, corrosive, and poisonous qualities, which attacks glass with avidity, but is insoluble in water. When cooled to a temperature of  $-187^\circ\text{C}$ ., it condenses to the liquid state in the form of a mobile yellow fluid with a characteristic odour something like that of chlorine, and at a still lower temperature it assumes an almost solid white form.

Fluorine attacks organic substances with violence ; acts strongly upon all metals (even gold and platinum to some extent), many of them passing into a state of inflammation when thrown in a finely divided state into the gas ; glass as well as water will burn in contact with fluorine.

**Hydrofluoric acid** ( $\text{HF}$ ) gas is made by warming a mixture of strong sulphuric acid and powdered calcium fluoride (fluorspar) in a lead or platinum vessel:  $\text{CaF}_2 + \text{H}_2\text{SO}_4 = \text{CaSO}_4 + 2\text{HF}$ , the evolved gas being collected in water, which solution is more commonly used than the gas. It can also be made by distillation of anhydrous acid potassium fluoride. It freezes at  $-83^\circ\text{C}$ ., and reacts with silica and silicates to form **silicon fluoride** ( $\text{SiF}_4$ ) gas.

Hydrofluoric acid is largely employed in the purification of graphite from silica, for etching glass, cleansing iron casting, and removing vitreous enamels from sheet steel. For etching purposes, as, for example, making the graduations on glass measuring apparatus, the object to be marked is coated with melted wax, and after tracing the design or marks on the coated glass, it is exposed to the action of the acid either in the form of gas or liquid, with the result that the glass is eaten into where exposed by the markings, the wax being unaffected. A mixture that can be used for etching glass is made by mixing equal weights of ammonium fluoride and dry precipitated barium sulphate together with hydrochloric acid and adding fuming hydrofluoric acid to a suitable consistency.

Hydrogen fluoride is an important catalyst in the alkylation process to combine olefin hydrocarbons, such as propylene, butylenes, and pentylenes, with an iso-paraffin hydrocarbon, such as isobutane, to form higher molecular weight branched chain hydrocarbons, called alkylate. Alkylate has a distillation range similar to gasoline, an octane number of 88 to 93, and responds well to addition of tetraethyl lead.

Hydrofluoric acid vapour is irritating and injurious to the respiratory organs, while the liquid produces ulcerated sores on the skin, especially

under the finger nails, and is, altogether, a very dangerous chemical compound. Prolonged washing in a stream of cold water is an effective remedy. The anhydrous acid is a limpid colourless liquid which boils at  $19.5^{\circ}\text{C}$ . For commercial purposes, aqueous solutions of this acid 30 per cent. and of 60 per cent. strength are produced, and the latter strength can be transported in steel drums. Bakelite receptacles are convenient for handling and measuring the solutions.

There are **fluorides** corresponding to the chlorides and also a number of double (or acid) fluorides. The fluorides of potassium, sodium, and iron are but sparingly soluble in water, while the fluorides of silver and tin are easily soluble. Most of the fluorides are easily fusible, and when ignited in a current of steam many of them are converted into oxides, hydrofluoric acid being evolved. Potassium and sodium fluorides ( $\text{KF}$  and  $\text{NaF}$ ) are used in compounding casein cement or the so-called "cold glues" and as preservatives for wood, etc.

Oxygen fluoride gas ( $\text{F}_2\text{O}$ ) has a boiling point of  $-167^{\circ}\text{C}$ .

Chlorine trifluoride ( $\text{ClF}_3$ ) is a liquid, almost as active as fluorine and a convenient way to handle that element. It "burns" glass wool as vigorously as gun-cotton burns.

Potassium hydrogen or acid fluoride, sometimes called bifluoride, is obtained in an anhydrous state by evaporation of a solution of potassium fluoride in aqueous hydrofluoric acid, followed by heating to  $110^{\circ}\text{C}$ ., and upon further heating to dull redness it is decomposed into the normal salt and hydrofluoric acid.

Sodium hydrogen or acid fluoride ( $\text{NaHF}_2$ ), or bifluoride, is a dry white substance, useful, in the form of a warm solution, for removing iron-mould.

Ammonium hydrogen or acid fluoride ( $\text{NH}_4\text{HF}_2$ ), or bifluoride, is a white crystalline body, soluble in water, used in alcohol manufacture for inhibiting the growth of acetic and lactic organisms, also as a brewery antiseptic; and in common with the corresponding potassium and sodium compounds for frosting glass.

Many of the double salts, such as antimony sodium fluoride ( $\text{NaSbF}_4$ ), are used as mordants instead of tartar emetic (see "Fluoremetic"). Sodium silicofluoride or fluosilicate ( $\text{Na}_2\text{SiF}_6$ ) finds use as an insecticide, and in the ceramic industries as a substitute for cryolite and as a preservative of rubber latex, while lead silicofluoride or fluosilicate ( $\text{PbSiF}_6$ ) (a very soluble salt) is used in the electrolytic refining of lead.

Calcium fluoride, which is practically insoluble, is used in the enamelled iron industry, and in the foundry. Chromium fluoride ( $\text{Cr}_2\text{F}_6 \cdot 8\text{H}_2\text{O}$ ), a green crystalline salt, is used to some extent in calico printing, and zinc fluoride ( $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ ) is used as a wood preservative.

The presence of fluorides in natural waters has been shown to be the cause of white spots developing on the teeth of children. See "Removal of Fluorides from Natural Waters by Defluorite," by Gladys Swope and R. H. Hess (*Ind. Eng. Chem.*, **29**, 424 (1937)); Churchill (U.S. Patent 2,059,553, Nov. 3, 1936); "Activated Alumina for Removing Fluorides from Drinking Water," by G. J. Fink and F. K. Lindsay (*Ind. Eng. Chem.*, **28**, 947 (1936)).

Many organic fluorides are known, both paraffinic and aromatic. (See "Freon.")

References: *Ind. Eng. Chem.*, **39**, 236-432 (March, 1947); **40**, 1615 (1948); *Fluorine Chemistry*, by J. H. Simons (Academic Press, New York).

**FLUORSPAR** — See Calcium (Fluoride).

**FLUOSILICATES** — See Fluorine, and Silicon.

**"FLÜSSIGGAS"** — That fraction of cracked oil gas available for transport by compression into steel cylinders at ordinary temperatures, which is reconverted into gas upon releasing the pressure; used for lighting of buoys, railway carriages, etc.

**FLUXES** — Substances or mixtures used to assist fusion by heat. One such flux is a mixture of nitre and tartar, and it is either placed in the crucible in which the mineral is to be fused or gradually introduced. The oxygen of the nitre causes the combustion of the carbon of the tartar and assists to raise the temperature of the mass. Potassium cyanide and other chemicals are used as fluxes according to the nature of the mineral or other substances to be fused.

"Black flux" is a mixture of potassium or sodium carbonate, sodium nitrate, and carbon, used in assaying; and "white flux" is a mixture of sodium carbonate with sodium nitrate and sodium nitrite, used in metallurgy and welding.

A flux and solder for use especially with cast-iron is made from 45 per cent. zinc chloride, 40 per cent. sal-ammoniac (ammonium chloride), and 15 per cent. metallic zinc. A patented flux for hard soldering is stated to consist of a mixture of borax and sodium phosphate melted at from 800° to 900° C. to a glassy mass.

A good flux for aluminium work and general purposes consists of potassium chloride 15 parts, sodium chloride 30 parts, lithium chloride 45 parts, potassium fluoride 7 parts, and potassium bisulphate 3 parts.

For brazing purposes, borax and boracic acid are variously employed, a mixture of the two substances being used in soldering rustless steels. Among other preparations used dry or in solution are zinc chloride for brass, copper, gun-metal and tin-plate; ammonium chloride for copper and iron; and hydrochloric acid for zinc and galvanized materials.

Resin is used for some soft alloys, turpentine for pewter and Britannia metal, palm oil and tallow for light or heavy lead work.

Fluxes are of great importance in metallurgical furnace work, since the addition of the proper fluxing materials permits the impurities (gangue) of the ore to be removed as liquid slag. (See *Fluxes and Slags in Metal Working and Melting* (The Faraday Society, London); also Alloys, Earth, Iron, Refractories, and Solders.)

**"FLUXRITE"** — Lead-tin solders that have the flux-paste entrapped longitudinally at several sections slightly within the surface instead of in the centre of the core, thus causing the flux to melt before the solder when heated.

**FCENUGREEK (Fenugreek)** — The seeds of *Trigonella Fœnum-græcum*,

a herb belonging to the N.O. Leguminosæ cultivated in India, Egypt, and Morocco. It is used in veterinary medicine, and is cultivated in India as a fodder plant.

**FOG** — See Air, and Mists.

**FOIL**, or thin sheet of metal, finds frequent use by chemists. Platinum foil is particularly useful, inasmuch as it is not acted upon by most chemicals, withstands exposure to high temperatures, and is consequently employed to test the behaviour of solid substances when exposed in crystal or powder form to heat, varying from low heating up to redness, for which purpose it is held by tongs or forceps. If, for instance, a small quantity of crystallized borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) be placed on a piece of platinum foil and heated over a Bunsen flame, it will be seen to swell up, lose its water of crystallization, and finally fuse to a clear glass-like appearance. Lead, copper, silver, gold, tin, zinc, aluminium, and magnesium are also prepared in the form of foil, and these find many artistic and utilitarian applications, especially in the food preparation and packaging industries.

**FOLIC ACID** — See Vitamins.

**FOODS** are the other substances which, in addition to water and air, serve to repair the various tissues of the body and to renew its energy. They are generally classified under the headings of proteins (albuminoid matters), carbohydrates (starch, sugar, etc.), and fats, although vegetable acids and mineral salts are essential to a perfect dietary, as also vitamins, and small amounts of hormones, which last are secreted in the body by certain glands. The general view is that starches, sugars, and fats give energy and heat, and that the growth-producing foods consist of dairy products and fleshy materials, vegetables, and fruits. Protein foods are requisite for the production of flesh. (See Cantor Lectures before the Royal Society of Arts on "Nutrition and National Health," by Major General Sir Robert McCarrison in 1936.)

Food values are calculated in calories (heat units), one of which represents the heat required to raise the temperature of one gram of water  $1^\circ\text{C}$ . Proteins and carbohydrates yield 4.1 calories per gram, while fats yield 9.3 calories per gram. While the food requirements of humans vary with the type and amount of work performed, the requirements for sedentary occupations is usually estimated as being between 2,000 and 2,500 calories per day. For active workers 3,000 to 3,500 are recommended, while individuals performing hard labour may require even more.

Even though the diet contains the required number of calories, there is no assurance that it will be adequate from the nutritional point of view. For proper utilization, vitamins (see same) must be present in adequate amounts. In addition, adequate diets must contain sufficient mineral elements, such as calcium, sodium, chlorine, etc., to maintain the body. For this reason, highly purified foods are not looked on with favour by nutrition workers; leafy vegetables and whole grain foods are recommended. A varied diet is considered essential for proper nutritive balance.

*References*: *An Introduction to Foods and Nutrition*, by Sherman and Lanford (Macmillan, London and New York); *Food Products*, by Sherman (Macmillan, London and New York).

**Food Refrigeration** — See Refrigeration.

**Food Canning** — See *Outlines of Food Technology*, by H. W. von Loesecke (Reinhold Publishing Corp., New York).

**Food Preservatives** — In general it is undesirable to use supplementary preservatives in food products, but occasionally such materials may be required. It has been established that many of the older preservatives such as formaldehyde, hydrofluoric acid and its salts and derivatives, borax, are dangerous to human health. Small quantities of sulphur dioxide, benzoic acid (and benzoates), and salicylic acid may be permitted in foodstuffs under certain conditions, but usually adequate preservation may be secured by heat sterilization and proper sanitation in the food plant.

Salt, vinegar, spices, wood smoke, etc., have been used for centuries for the preservation of many foods. The use of these materials is not considered to be harmful to health.

**Frozen Foods** — "Quick-frozen" fruits, vegetables, and meats are now available. The rapid freezing process preserves the natural flavours, textures, and food values of these important foods, and their use will undoubtedly increase.

*References*: Food Number, *Chem. and Ind.*, **51**, 81 (1932); L. H. Lampitt on "Science and Food," *Chem. and Ind.*, **51**, 238 (1932); "Food Fakes," by E. G. Jones (lecture, Institute of Chemistry); Reports of the Food Investigation Board (H.M. Stationery Office); *Food Preservation*, by W. W. Chenoweth (Chapman and Hall, London); *The Bacteriology of Food*, by C. Dukes (H. K. Lewis and Co., London); *Foods: their Composition and Analysis*, by A. and M. Wynter Blyth (C. Griffin and Co., London); *Analyses and Energy Values of Foods*, by R. H. A. Plimmer (H.M. Stationery Office); *The Chemical Analysis of Foods*, by Cox (J. and A. Churchill, London); *Structure and Composition of Foods*, by A. L. and K. B. Winton (Chapman and Hall, London); *Manual of Industrial Nutrition*, Food Distribution Administration, Washington, D.C.; *Outlines of Food Technology*, by H. W. von Loesecke (Reinhold Publishing Corp., New York); *Drying and Dehydration of Foods*, by H. W. von Loesecke (Reinhold Publishing Corp., New York); *Chemistry of Food and Nutrition*, by H. C. Sherman (Macmillan Co., New York); *The Chemistry and Technology of Food and Food Products*, by Morris B. Jacobs (Interscience Publishers, New York); *Colloid Aspects of Food Chemistry and Technology*, by W. Clayton (J. and A. Churchill, London); *Index to the Literature of Food Investigation*, by Miss Glennie (H.M. Stationery Office); proceedings of the Food Group of the Society of Chemical Industry appearing in *Chemistry and Industry*; section on "Foods" in *Annual Reports of the Progress of Applied Chemistry* (Society of Chemical Industry); Feeding Stuffs, Proteins, Refrigeration, Vitamins, and Wheat.

**FORENSIC CHEMISTRY** — See *Forensic Chemistry and Scientific Criminal Investigation*, by A. Lucas (E. Arnold and Co., London).

**FORMALDEHYDE (Formalin, Methyl Aldehyde, or Methanal (H.CHO))** is a gas soluble in water, which liquefies at  $-21^{\circ}$  C. to a colourless solution of density 0.815, solidifies at  $-92^{\circ}$  C., and has a very irritating action on the mucous membranes of the eyes, nose and throat. An aqueous solution of 40 per cent. strength is an article of commerce, largely used under the name of Formalin for disinfecting and preservative purposes; and to reduce the toxicity of bacterial toxins so that they are harmless to the human patient. It is made by passing a current of methyl alcohol vapour admixed with air over a glowing platinum or copper spiral or netting, and absorption of the resulting gas in water.

It is also obtained, together with methyl alcohol, by the oxidation of methane, using carbon dioxide, the mixed gases being heated under suitable conditions to  $500^{\circ}$  to  $700^{\circ}$  C., and the products of the interaction rapidly cooled. Under favourable conditions, the yield of formaldehyde is stated to amount to about 56 per cent. calculated on the methane used, the yield of methyl alcohol being favoured by slow passage of the gases.

Formaldehyde possesses the property of making gelatine and glue insoluble in water, and this is utilized in many technical applications, including tanning, the preservation of adhesives and anatomical specimens. It is also used in making phenol-formaldehyde resins and those of similar type, such as "Bakelite," "Formite," "Galilith," "Margalite," "Resinite," etc. (See Gums and Resins (Synthetic).)

Among other applications may be mentioned its uses in the treatment of certain dyestuffs on the fibre to make them fast to washing and milling, hardening leather, in waterproofing, as a reducing agent, and in the recovery of rare metals. Its employment as a food preservative is prohibited on account of its poisonous character. (See Foods.)

The polymeric solid white paraform is more useful for disinfecting rooms by fumigation, as it is easily vaporized, and equally effective per unit of active agent. (See Paraform, and Fumigation.)

Formaldehyde undergoes condensation when heated under 2 atmospheres pressure in aqueous solution in presence of magnesium oxide, the primary change leading to the production of methyl alcohol and formic acid; somewhat later, sugars are formed. It is believed to play an important part in the process of plant assimilation, and glycerine has been synthesized from it.

The products resulting from formaldehyde condensations with aromatic amines, phenols, and aromatic hydrocarbons are of value in respect of their bearing on the production of various industrial products, such as organic colouring matters, synthetic drugs, and artificial resins. The object of the earlier workers was to produce substitutes for shellac, but the peculiar properties of these products, notably their resistance to heat, electricity, and chemical action, have led to their adoption for many other purposes. Some of the reactions with acid condensing agents lead to the production of fusible soluble resins of the "Novolak" type, while alkaline catalytic reagents favour the formation of insoluble resinoids. Air-drying varnishes and

lacquers can be obtained from some of them. Synthetic resin varnishes are largely used as stoving varnishes, and for coating insulating fabrics and tapes used in the electrical industry. (See *Formaldehyde*, by J. F. Walker (Reinhold Publishing Corp., New York) ; and Gums and Resins (Synthetic).)

**FORMALIN** — See Formaldehyde.

**FORMAMIDE** (Du Pont) ( $\text{HCONH}_2$ ) — A colourless, odourless, hygroscopic liquid, decomposing at  $180^\circ\text{C}$ . Used as a solvent, and in chemical syntheses.

**FORMIC ACID** ( $\text{H.COOH}$ ) occurs naturally in ants, in the sting of nettles, bees, and wasps, in the processionary caterpillar, the fruit of the soap-tree (*Sapindus saponaria*), fir needles and tamarinds, and is also formed as a by-product in the atmospheric oxidation of turpentine. When pure, it is a colourless liquid of sp. gr. 1.220, m.p.  $8.6^\circ\text{C}$ ., b.p.  $100.8^\circ\text{C}$ ., and fumes in the air. It is a powerful antiseptic, very corrosive, and mixes with water in all proportions. The chief commercial source of formic acid is sodium formate made by the reaction of carbon monoxide and sodium hydroxide under pressure with heating, and this, by interaction with sulphuric acid, yields formic acid of 90 per cent. strength. From this, the anhydrous acid can be obtained by distillation with strong sulphuric acid under reduced pressure. The Carter and Bredig process for making formic acid is by the direct union of hydrogen and carbon dioxide, using pressure and palladium as a catalyst.

For commercial purposes formic acid is prepared of 85 per cent. strength, and finds industrial applications in the electroplating, in the tanning trade, and in the textile industry in dyeing cotton and woollen fibres. It slowly decomposes on storage, and much more readily upon heating. It is also decomposed by strong sulphuric acid into carbon monoxide and water, while in aqueous solution it is oxidized by the halogens into carbon dioxide and halogen acid, and is also subject to photochemical decomposition. Formic acid is broken down by *B. coli* in two ways—anaerobically to  $\text{H}_2 + \text{CO}_2$  and aerobically to  $\text{H}_2\text{O} + \text{CO}_2$ .

The formates are converted by heat into oxalates and hydrogen. (See "Alacet.")

"**FORMITE**" — A proprietary phenol-formaldehyde product. (See "Bakelite.")

**FORMOLITE RESINS** — See Gums and Resins (Synthetic).

**FORMOSE** ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) — A mixture of monosaccharides obtained by the action of alkaline condensing agents, such as lime-water, on formaldehyde, of which formose is a mixture of polymers.

"**FORMOSUL**" — See Hydrosulphites.

**FORMULAS** — The arrangement of symbols representing the chemical composition of substances. The symbols which are used are explained in the several sections dealing with Chemical Compounds, Chemical Interactions, and Elements. Formulas are of various types. The ordinary formula indicates the composition without respect to any particular molecular arrangement or structure ; thus  $\text{NaCl}$  expresses

a herb belonging to the N.O. Leguminosæ cultivated in India, Egypt, and Morocco. It is used in veterinary medicine, and is cultivated in India as a fodder plant.

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**FOLIC ACID** — See Vitamins.

**FOODS** are the other substances which, in addition to water and air, serve to repair the various tissues of the body and to renew its energy. They are generally classified under the headings of proteins (albuminoid matters), carbohydrates (starch, sugar, etc.), and fats, although vegetable acids and mineral salts are essential to a perfect dietary, as also vitamins, and small amounts of hormones, which last are secreted in the body by certain glands. The general view is that starches, sugars, and fats give energy and heat, and that the growth-producing foods consist of dairy products and fleshy materials, vegetables, and fruits. Protein foods are requisite for the production of flesh. (See Cantor Lectures before the Royal Society of Arts on "Nutrition and National Health," by Major General Sir Robert McCarrison in 1936.)

Food values are calculated in calories (heat units), one of which represents the heat required to raise the temperature of one gram of water  $1^\circ\text{C}$ . Proteins and carbohydrates yield 4.1 calories per gram, while fats yield 9.3 calories per gram. While the food requirements of humans vary with the type and amount of work performed, the requirements for sedentary occupations is usually estimated as being between 2,000 and 2,500 calories per day. For active workers 3,000 to 3,500 are recommended, while individuals performing hard labour may require even more.

Even though the diet contains the required number of calories, there is no assurance that it will be adequate from the nutritional point of view. For proper utilization, vitamins (see same) must be present in adequate amounts. In addition, adequate diets must contain sufficient mineral elements, such as calcium, sodium, chlorine, etc., to maintain the body. For this reason, highly purified foods are not looked on with favour by nutrition workers; leafy vegetables and whole grain foods are recommended. A varied diet is considered essential for proper nutritive balance.

*References: An Introduction to Foods and Nutrition*, by Sherman and Lanford (Macmillan, London and New York); *Food Products*, by Sherman (Macmillan, London and New York).

**Food Refrigeration** — See Refrigeration.

**Food Canning** — See *Outlines of Food Technology*, by H. W. von Loesecke (Reinhold Publishing Corp., New York).

**Food Preservatives** — In general it is undesirable to use supplementary preservatives in food products, but occasionally such materials may be required. It has been established that many of the older preservatives such as formaldehyde, hydrofluoric acid and its salts and derivatives, borax, are dangerous to human health. Small quantities of sulphur dioxide, benzoic acid (and benzoates), and salicylic acid may be permitted in foodstuffs under certain conditions, but usually adequate preservation may be secured by heat sterilization and proper sanitation in the food plant.

Salt, vinegar, spices, wood smoke, etc., have been used for centuries for the preservation of many foods. The use of these materials is not considered to be harmful to health.

**Frozen Foods** — "Quick-frozen" fruits, vegetables, and meats are now available. The rapid freezing process preserves the natural flavours, textures, and food values of these important foods, and their use will undoubtedly increase.

*References: Food Number, Chem. and Ind.*, **51**, 81 (1932); L. H. Lampitt on "Science and Food," *Chem. and Ind.*, **51**, 238 (1932); "Food Fakes," by E. G. Jones (lecture, Institute of Chemistry); Reports of the Food Investigation Board (H.M. Stationery Office); *Food Preservation*, by W. W. Chenoweth (Chapman and Hall, London); *The Bacteriology of Food*, by C. Dukes (H. K. Lewis and Co., London); *Foods: their Composition and Analysis*, by A. and M. Wynter Blyth (C. Griffin and Co., London); *Analyses and Energy Values of Foods*, by R. H. A. Plimmer (H.M. Stationery Office); *The Chemical Analysis of Foods*, by Cox (J. and A. Churchill, London); *Structure and Composition of Foods*, by A. L. and K. B. Winton (Chapman and Hall, London); *Manual of Industrial Nutrition*, Food Distribution Administration, Washington, D.C.; *Outlines of Food Technology*, by H. W. von Loesecke (Reinhold Publishing Corp., New York); *Drying and Dehydration of Foods*, by H. W. von Loesecke (Reinhold Publishing Corp., New York); *Chemistry of Food and Nutrition*, by H. C. Sherman (Macmillan Co., New York); *The Chemistry and Technology of Food and Food Products*, by Morris B. Jacobs (Interscience Publishers, New York); *Colloid Aspects of Food Chemistry and Technology*, by W. Clayton (J. and A. Churchill, London); *Index to the Literature of Food Investigation*, by Miss Glennie (H.M. Stationery Office); proceedings of the Food Group of the Society of Chemical Industry appearing in *Chemistry and Industry*; section on "Foods" in *Annual Reports of the Progress of Applied Chemistry* (Society of Chemical Industry); Feeding Stuffs, Proteins, Refrigeration, Vitamins, and Wheat.

**FORENSIC CHEMISTRY** — See *Forensic Chemistry and Scientific Criminal Investigation*, by A. Lucas (E. Arnold and Co., London).

**FORMALDEHYDE (Formalin, Methyl Aldehyde, or Methanal ( $\text{H}\cdot\text{CHO}$ ))** is a gas soluble in water, which liquefies at  $-21^{\circ}\text{C}$ . to a colourless solution of density 0.815, solidifies at  $-92^{\circ}\text{C}$ ., and has a very irritating action on the mucous membranes of the eyes, nose and throat. An aqueous solution of 40 per cent. strength is an article of commerce, largely used under the name of Formalin for disinfecting and preservative purposes; and to reduce the toxicity of bacterial toxins so that they are harmless to the human patient. It is made by passing a current of methyl alcohol vapour admixed with air over a glowing platinum or copper spiral or netting, and absorption of the resulting gas in water.

It is also obtained, together with methyl alcohol, by the oxidation of methane, using carbon dioxide, the mixed gases being heated under suitable conditions to  $500^{\circ}$  to  $700^{\circ}\text{C}$ ., and the products of the interaction rapidly cooled. Under favourable conditions, the yield of formaldehyde is stated to amount to about 56 per cent. calculated on the methane used, the yield of methyl alcohol being favoured by slow passage of the gases.

Formaldehyde possesses the property of making gelatine and glue insoluble in water, and this is utilized in many technical applications, including tanning, the preservation of adhesives and anatomical specimens. It is also used in making phenol-formaldehyde resins and those of similar type, such as "Bakelite," "Formite," "Galilith," "Margalite," "Resinite," etc. (See Gums and Resins (Synthetic).)

Among other applications may be mentioned its uses in the treatment of certain dyestuffs on the fibre to make them fast to washing and milling, hardening leather, in waterproofing, as a reducing agent, and in the recovery of rare metals. Its employment as a food preservative is prohibited on account of its poisonous character. (See Foods.)

The polymeric solid white paraform is more useful for disinfecting rooms by fumigation, as it is easily vaporized, and equally effective per unit of active agent. (See Paraform, and Fumigation.)

Formaldehyde undergoes condensation when heated under 2 atmospheres pressure in aqueous solution in presence of magnesium oxide, the primary change leading to the production of methyl alcohol and formic acid; somewhat later, sugars are formed. It is believed to play an important part in the process of plant assimilation, and glycerine has been synthesized from it.

The products resulting from formaldehyde condensations with aromatic amines, phenols, and aromatic hydrocarbons are of value in respect of their bearing on the production of various industrial products, such as organic colouring matters, synthetic drugs, and artificial resins. The object of the earlier workers was to produce substitutes for shellac, but the peculiar properties of these products, notably their resistance to heat, electricity, and chemical action, have led to their adoption for many other purposes. Some of the reactions with acid condensing agents lead to the production of fusible soluble resins of the "Novolak" type, while alkaline catalytic reagents favour the formation of insoluble resinoids. Air-drying varnishes and

lacquers can be obtained from some of them. Synthetic resin varnishes are largely used as stoving varnishes, and for coating insulating fabrics and tapes used in the electrical industry. (See *Formaldehyde*, by J. F. Walker (Reinhold Publishing Corp., New York); and Gums and Resins (Synthetic).)

**FORMALIN** — See Formaldehyde.

**FORMAMIDE** (Du Pont) ( $\text{HCONH}_2$ ) — A colourless, odourless, hygroscopic liquid, decomposing at  $180^\circ\text{C}$ . Used as a solvent, and in chemical syntheses.

**FORMIC ACID** ( $\text{H.COOH}$ ) occurs naturally in ants, in the sting of nettles, bees, and wasps, in the processionary caterpillar, the fruit of the soap-tree (*Sapindus saponaria*), fir needles and tamarinds, and is also formed as a by-product in the atmospheric oxidation of turpentine. When pure, it is a colourless liquid of sp. gr. 1.220, m.p.  $8.6^\circ\text{C}$ ., b.p.  $100.8^\circ\text{C}$ ., and fumes in the air. It is a powerful antiseptic, very corrosive, and mixes with water in all proportions. The chief commercial source of formic acid is sodium formate made by the reaction of carbon monoxide and sodium hydroxide under pressure with heating, and this, by interaction with sulphuric acid, yields formic acid of 90 per cent. strength. From this, the anhydrous acid can be obtained by distillation with strong sulphuric acid under reduced pressure. The Carter and Bredig process for making formic acid is by the direct union of hydrogen and carbon dioxide, using pressure and palladium as a catalyst.

For commercial purposes formic acid is prepared of 85 per cent. strength, and finds industrial applications in the electroplating, in the tanning trade, and in the textile industry in dyeing cotton and woollen fibres. It slowly decomposes on storage, and much more readily upon heating. It is also decomposed by strong sulphuric acid into carbon monoxide and water, while in aqueous solution it is oxidized by the halogens into carbon dioxide and halogen acid, and is also subject to photochemical decomposition. Formic acid is broken down by *B. coli* in two ways—anaerobically to  $\text{H}_2 + \text{CO}_2$  and aerobically to  $\text{H}_2\text{O} + \text{CO}_2$ .

The formates are converted by heat into oxalates and hydrogen. (See "Alacet.")

"**FORMITE**" — A proprietary phenol-formaldehyde product. (See "Bakelite.")

**FORMOLITE RESINS** — See Gums and Resins (Synthetic).

**FORMOSE** ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) — A mixture of monosaccharides obtained by the action of alkaline condensing agents, such as lime-water, on formaldehyde, of which formose is a mixture of polymers.

"**FORMOSUL**" — See Hydrosulphites.

**FORMULAS** — The arrangement of symbols representing the chemical composition of substances. The symbols which are used are explained in the several sections dealing with Chemical Compounds, Chemical Interactions, and Elements. Formulas are of various types. The ordinary formula indicates the composition without respect to any particular molecular arrangement or structure; thus  $\text{NaCl}$  expresses

the combination of 1 atom weight of sodium with 1 atom weight of chlorine in 1 mole weight of sodium chloride. Again, the formula  $(\text{NH}_4)_2\text{SO}_4$  expresses the combination of 2 group weights of ammonium with 1 group weight of sulphate in 1 mole weight of ammonium sulphate.

The **Empirical Formula** of a substance is ascertained from the results of its analysis, the percentages of elements found present being divided by their atomic weights. For example, hydrocyanic acid upon analysis is shown to contain as follows :

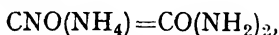
Hydrogen	..	..	..	..	3.704	per cent.
Carbon	..	..	..	..	44.444	„
Nitrogen	..	..	..	..	51.852	„

and if these percentages are divided by the atomic weights of the three elements,  $\text{H}=1$ ,  $\text{C}=12$ , and  $\text{N}=14$  respectively, it will be found that the quotients are practically identical, so that the component elements are combined in the proportions of one each thus,  $\text{HCN}$ , which is the simplest formula of the substance.

Or again, taking salt (sodium chloride), it yields upon analysis 39.316 per cent. sodium and 60.684 per cent. chlorine, and the division of these numbers by the atomic weights 23 and 35.5 shows the two components to be contained in the elemental proportions, so that the empirical formula is  $\text{NaCl}$ .

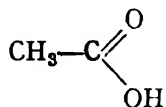
**Molecular Formulas** can be ascertained only for those substances that permit a determination of their molecular weight. This includes gases and volatilizable compounds, and those that dissolve in any solvent to form a true solution. When the molecular weight has been ascertained by known approved methods, then by combining this weight with the information contained in the empirical formula, the molecular formula is obtained. Many chemical formulas are molecular formulas ; in some cases, however, the empirical formula, which is the simplest formula, is used because of our lack of further knowledge.

**Constitutional or Rational Formulas**, on the other hand, are used to express a sense of construction or structure, as when, for example, ammonium cyanate is resolved by heating into urca, the change may be expressed as follows :



in order to show that, although empirically the composition of the two substances is the same, both being concretely expressed by the formula  $\text{CN}_2\text{H}_4\text{O}$ , the molecular arrangements or structures are different.

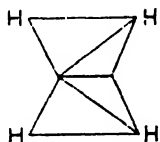
Again, the empirical formula of ethyl alcohol is  $\text{C}_2\text{H}_6\text{O}$ , but when expressed constitutionally as  $\text{C}_2\text{H}_5(\text{OH})$ , it is seen that the molecule has an alcoholic structure and that the group  $\text{OH}$  may be replaced or substituted by other groups. So also acetic acid of empirical formula  $\text{C}_2\text{H}_4\text{O}_2$  may be expressed constitutionally in several ways, thus :



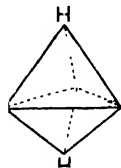
—that is, carbon in association with the groupings  $\text{CH}_3, \text{OH}, \text{O}$  ; otherwise as  $\text{CH}_3, \text{CO}, \text{OH}$ —that is, the radical methyl, the radical hydroxyl, and oxygen all in direct combination with carbon ; or as  $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ —that is, as hydrogen acetate or a molecule of hydrogen in which 1 atom is replaced by the group  $\text{C}_2\text{H}_3\text{O}_2$ , according to the views taken of the order of arrangements of the atoms in the acetic acid molecule.

The bonds or attachments between atoms as existing in compounds are represented by dots (.) or lines (—), for example, water may be represented either as  $\text{H}_2\text{O}$  or  $\text{H.O.H}$  or  $\text{H—O—H}$  ; double and triple bonds being represented similarly, for example,  $\text{H}_2\text{C} : \text{CH}_2$  (ethylene) and  $\text{HC} : \text{N}$ , or  $\begin{smallmatrix} \text{H} \\ > \text{C} = \text{C} < \\ \text{H} \end{smallmatrix}$  and  $\text{H—C} \equiv \text{N}$ .

**Space Formulas** are used to give a figurative view of the structure of compounds in three dimensions, and are chiefly employed in connection with carbon compounds ; thus ethylene ( $\text{CH}_2=\text{CH}_2$ ) and acetylene ( $\text{CH} \equiv \text{CH}$ ) are figuratively shown respectively as follows (assuming a carbon atom in the centre of each tetrahedron) :



2 regular tetrahedra, edge to edge, with H at each of the 4 free corners.



2 regular tetrahedra, base to base, with H at each of the 2 free corners.

For more extended discussion consult *Van Nostrand's Scientific Encyclopædia* (D. Van Nostrand Co., New York ; Chapman and Hall, London), articles on Chemical Formulas, and Chemical Nomenclature. (See also Atoms, Benzene Ring, Chemical Interactions, Co-ordination, Rings, Stereo-chemistry, and Valencies.)

“ **FOUADIN** ” — See Stibophen.

**FOULING FACTOR** — See Heat Transfer.

“ **FOURNEAU 309** ” — See Suramin.

**FRACTIONATING COLUMN** — See Distillation.

**FRANCIUM** (Fr) — Element number 87, discovered by Mlle M. Perey, in 1940, as a very rare component of the actinium radioactive series, and accepted (1949) by the International Union of Chemistry. Francium is a member of the alkali group, of which sodium and potassium are the familiar elements. Francium 223 is formed by alpha particle decay of actinium 227, and francium 221 (1) by alpha particle decay of actinium 225, and (2) as a decay product of a sequence starting with artificial thorium 233. (See Nuclear Chemistry.)

**FRANGULA** (Alder Buckthorn Bark, Persian Berries) — The dried bark of *Rhamnus Frangula*, a shrub growing throughout Europe and Siberia. It contains a glycoside which, on hydrolysis, yields rhamnose and frangula-emodin and possesses laxative properties.

## 444 FRANKINCENSE — FRIEDEL-CRAFTS REACTION

**FRANKINCENSE** — See Gums (Olibanum).

**FRANKLINITE** — An iron-manganese-zinc ore found in New Jersey (U.S.A.), Southland (Australia), and elsewhere, having the composition  $(\text{ZnFeMn})\text{O}$ ,  $(\text{FeMn})_2\text{O}_3$ , containing about 67 parts iron oxide, 17 parts manganese oxide, and 16 parts oxide (crystal system No. 1, and sp. gr. 5.0).

**"FRARY METAL"** — An alloy of lead, calcium, and barium made by the electrodeposition of calcium and barium in molten lead; stated to be particularly useful as a bearing metal.

**FRAXIN** — See Glycosides.

**FREE RADICALS** — See Radicals.

**FREEZING MIXTURES** — See Refrigeration.

**FREEZING-POINTS** — The temperature at which liquids solidify upon cooling. The freezing-point of a pure substance is not necessarily the same as the melting-point of that substance, since supercooling may and usually does occur. The melting-point is the more commonly used constant for pure substances. According to the law of Raoult, the freezing-point of a solution is depressed to the same extent when equal molecular quantities of various substances are dissolved in identical weights of the same solvent. (See Crystals (Supercooling), and Melting Points.)

**FRENCH CHALK (Steatite or Soap-Stone)** — A soft silicate of magnesium mineral, talc-like in nature, used in the engraving and lithographing trades, in preparing size for rope and twine-making, in preparing crayons, paper-making, etc. A large deposit, which can be cut, sawn, drilled, and polished, and will absorb many colours, is located at Zwettl near the Bohemian frontier. (See Steatite, and Talc.)

**FRENCH POLISH** — A solution of shellac in alcohol, other resins being sometimes incorporated.

**"FREON"** — Trade-mark for a group of halogenated methane derivatives, used as refrigerants and as propellant ("F-12") in aerosol insecticides.

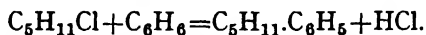
"F-11"	$(\text{CCl}_3\text{F})$ ,	b.p. $74.7^\circ \text{F}$ .	at 1 atm.
"F-12"	$(\text{CCl}_2\text{F}_2)$ ,	" $-21.6^\circ \text{F}$ .	"
"F-21"	$(\text{CHCl}_2\text{F})$ ,	" $48^\circ \text{F}$ .	"
"F-22"	$(\text{CHClF}_2)$ ,	" $-41.4^\circ \text{F}$ .	"
"F-113"	$(\text{C}_2\text{Cl}_3\text{F}_3)$ ,	" $117.6^\circ \text{F}$ .	"
"F-114"	$(\text{C}_2\text{Cl}_2\text{F}_4)$ ,	" $38.4^\circ \text{F}$ .	"

**FRIAR'S BALSAM** — See Balsams.

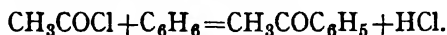
**FRIEDEL-CRAFTS REACTION** — This is a reaction which brings about the formation of carbon to carbon links, using, as intermediates, a hydrocarbon and an alkyl halide or an acid chloride. The most generally used catalyst is anhydrous aluminium chloride, although

others are used, such as anhydrous ferric chloride, stannic chloride, or liquid hydrofluoric acid.

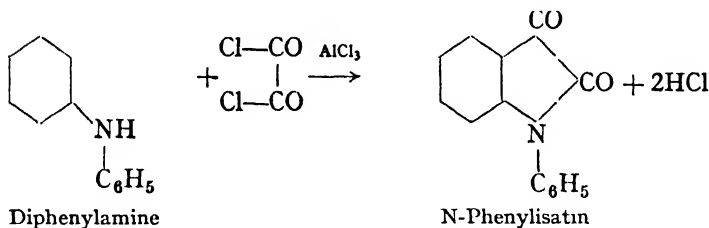
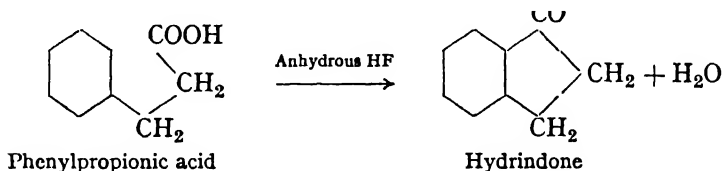
**Hydrocarbon Synthesis.** In this type of reaction an alkyl halide is used, *e.g.*, if a solution of amyl chloride in benzene is treated with aluminium chloride, amyl benzene is formed and hydrogen chloride is liberated, thus :



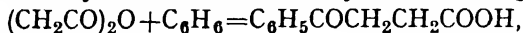
**Ketone Synthesis.** If a mixture of acetyl chloride and benzene is treated with anhydrous aluminium chloride, benzophenone is formed, and hydrogen chloride is liberated, thus :



There are many modifications of the Friedel-Crafts reaction, for instance, ring compounds may be prepared by the intramolecular elimination of water from an acid *e.g.*



Cyclic anhydrides yield keto acids with hydrocarbons, *e.g.*,



Succinic anhydride

Benzoyl propionic acid

and, in fact, acid anhydrides can usually be employed in place of the corresponding acyl halide.

In the hydrocarbon synthesis only catalytic amounts of aluminium chloride are required, but when acyl halides, or anhydrides, are used, then over one molecular proportion has to be used, as the carbonyl group forms a complex with the  $\text{AlCl}_3$ , thus removing it from the sphere of action. Aliphatic hydrocarbons do not react with halides, *e.g.*, pentane will not react with chlorobenzene to form amyl benzene. Another disadvantage of the method for alkylation is that it does not usually stop at one stage, a mixture of products being obtained. (See *Anhydrous Aluminium Chloride in Organic Chemistry*, by Charles A. Thomas (Reinhold Publishing Corp., New York).)

prospect of finding natural petroleum is considered to be unlikely. The shale oil industry should be encouraged, but requires an economical process to be discovered for the removal of sulphur. The gas and coke industries have a capacity for supplying oil which is governed by the demand for their principal products. Very significantly, low temperature carbonization must be ignored as a major source of oil. The conclusion is that the only methods that can be considered as offering potentially valuable sources of large supplies of oil are those of hydrogenation and synthesis.

Subsequent studies have been carried on and the results appear in *Fuel Research 1939 to 1946* (H.M.S.O., London). Reports are given there on (1) the recovery of pyrites from coal, (2) the production of hydrogen gas, (3) the hydrogenation of coal and tar, and (4) the deposition of solid matter on the external surfaces of boilers at power stations.

In using fuel oil as a heating agent it is atomized with the necessary quantity of air to make the mixture combustible, and there are three distinct systems of application—viz., by means of compressed air (air-jet system), the steam-jet system, and the pressure-jet system, in which the oil is sprayed under pressure by means of a steam-driven pump, this latter being recognized as the most economical. In some cases powdered coal is used in association with the oil.

See lecture by A. E. Dunstan on "Fluid Fuels" (*Chem. and Ind.*, 51, 822, 846 (1932)); J. S. S. Brame on "Colloidal or Coal-Oil Fuel" (*Chem. and Ind.*, 51, 855 (1932)); U.S. Bureau of Mines (Pittsburgh, Pennsylvania) on *Synthetic Liquid Fuels*: R. I. 4651, Oil from Coal; R. I. 4652, Oil from Oil Shale; R. I. 4653, Liquid Fuel from Agricultural Residues; R. I. 4654, Oil from Secondary Recovery and Refining; Coal, Fuel (Colloidal), Methyl Alcohol, Petroleum, and "Synthol."

**FUEL (Powdered)** — See Coal.

**FUEL OIL** — See Fuel (Liquid).

**FUELS** — Fuels are generally classified, on the basis of their states of aggregation, into (1) solid fuels, (2) liquid fuels, and (3) gaseous fuels. This classification is also supported by the manner of burning fuels, which depends far more upon the state than the composition of fuels. Solids require, in general, grates to support the fuels, up through which grates and fuels the air required for burning can pass. Liquids do not need grates, but must, however, be atomized in a manner that will result in satisfactory mixing with air. Gases do not require atomizing, simply efficient mixing with air, and, therefore, gases call for the simplest mechanical equipment for combustion. Except in those regions such as central U.S.A., gaseous fuels can usually not compete economically with other classes of fuels. Producer gas is, however, competitive.

1. Solid fuels: Coal (see same) is easily in a class by itself among solid fuels in respect to demand due to its wide distribution and ready availability in most industrial sections of the world. Coke has important uses (see same). Wood is of local interest.

## WORLD FUEL PRODUCTION

ESTIMATED AVERAGE PER ANNUM, 1933-35

Authority : *Minerals Yearbook* (United States Bureau of Mines)

Data arranged by the Editor.

COUNTRY	COAL		CRUDE PETROLEUM	
	10 <sup>6</sup> Long Tons	Imports Per cent. of Consumption	10 <sup>6</sup> Long Tons	Imports Per cent. of Consumption
Belgium .. ..	26.4	17	0.1	100
France .. ..	70.1	24	4.2	98
Germany .. ..	242.8	2	0.7	52
Italy .. ..	11.8	93	0.2	89
Japan .. ..	38.7	1	2.8	92
U.S.S.R. (Russia) ..	87.8	<0.5	22.9	0
United Kingdom ..	161.1	<0.5	1.9	94
United States ..	352.5	<0.5	125.3	4
8 Countries, above	991.2	{ Produced 85% Consumed 80%	158.1	{ Produced 72% Consumed 75%
WORLD'S TOTAL ..	1233.3		209.7	

"Coal is probably the only primary industrial mineral of which Japan has sufficient reserves."—*Minerals Yearbook*, 1937, p. 100.

## COAL RESERVES OF THE UNITED KINGDOM

Date	Proved	Unproved	Total	Authority
1871	90,207	56,273	146,480 million short tons	Report of the Royal Commission on Coal Supplies
1905	100,915	39,483	140,398 million short tons	Report of the Royal Commission on Coal Supplies
1913	133,117	45,610	178,727 million long tons	Report of the 12th International Geological Congress, Toronto
1915	136,000	61,000	197,000 million long tons	H. S. Jevons, <i>The British Coal Trade</i> (Kegan, Paul, Trench and Trübner)
1925			(Review of the situation)	Report of the Royal Commission on the Coal Industry

Note :—A reasonable estimate of the total coal production of the United Kingdom to the end of 1934 is approximately 18,000 million long tons, and the average annual production during the ten-year period 1927 to 1936 is approximately 230 million long tons.

See Second Hinchley Memorial Lecture on "Our National Coal Resources," by Sir Harold Hartley (*Trans. Inst. Chem. Eng.*, 13, 158 (1935)), in addition to the following references (p. 450).

# ENERGY SUPPLIED FROM MINERAL FUELS AND WATER POWER IN THE UNITED STATES BY YEARS

Authority : *Minerals Year Book* (United States Bureau of Mines)

Data selected by the Editor. All data in trillions (10<sup>12</sup>) of B.Th.U.

Water power calculated at the prevailing central-station equivalent in fuel for each year.

Year	Coal	Petroleum	Natural Gas	Total Mineral Fuels	Water Power	Total
1889	3,746	211	268	4,225	?	?
1899	6,708	342	240	7,291	238	7,529
1904	9,291	702	333	10,326	354	10,680
1909	12,155	1,099	517	13,771	513	14,284
1914	13,545	1,696	636	15,877	636	16,513
1916	15,548	1,930	810	18,288	681	18,969
1918	17,868	2,362	775	21,005	701	21,706
1920	17,336	3,295	858	21,489	738	22,227
1922	12,551	4,109	820	17,480	643	18,123
1924	15,064	4,751	1,228	21,042	648	21,690
1926	17,319	4,987	1,411	23,717	728	24,445
1928	15,169	5,888	1,686	22,743	854	23,597
1930	14,136	5,761	2,089	21,986	752	22,738
1932	9,470	4,979	1,673	16,122	713	16,835
1934	10,970	5,661	1,904	18,535	698	19,233
1936	12,989	6,792	2,330	22,111	812	22,923
1939	11,745	7,789	2,663	22,197	838	23,035
1942	16,908	8,394	3,282	28,584	1,136	29,720
1945	16,576	10,712	3,662	30,950	1,399	32,349
1947	18,100	11,700	4,800	34,600	1,400	36,000

Public utility central station electric power plants, U.S.A., have increased in fuel efficiency at a remarkable rate as the following record shows :

1889	7.0	pounds of coal per kilowatt hour.
1913	4.0	" " " "
1925	2.2	" " " "
1941	1.3	" " " "
1947	1.3	" " " "

2. Liquid fuels : Petroleum (see same) stands among liquid fuels on a par with coal among solid fuels, that is, supreme in its field. (See Fuel (Liquid), and Motor Spirit.)

3. Gaseous fuels are many and of diversified composition. (See Coke Gas (Coal), Water Gas, and Producer Gas.)

**References :** Reports of the Fuel Research Board (H.M. Stationery Office, London) ; *Fuel : Solid, Liquid, and Gaseous*, by J. S. S. Brame (Ed. Arnold and Co., London) ; *Fuel*, by G. W. Andrew (E. Benn, Ltd., London) ; *Technical Data on Fuel*, edited by H. M. Spiers ; *Transactions of the World Fuel Conference* (Lund Humphries) ; *The Efficient Use of Fuel* (H.M. Stationery Office, London) ; *A.S.T.M. Manual of Engine Test Methods for Rating Fuels* (American Society for Testing Materials, Philadelphia) ; *Fuels, Combustion, and Furnaces*, by John Griswold (McGraw-Hill Book Co., New York) ; Haslam and Russell, *Fuels and Their Combustion* (McGraw-Hill Book Co., New York) ; *Fuels and Combustion Handbook*, by A. J. Johnson and G. H. Auth (McGraw-Hill Book Co., New York) ; *Fuel* (a journal of fuel science) (Interscience Publishers, New York) ; Ashes, Berginization, Coal, Coke, Combustion, Fuel (Colloidal), Fuel (Liquid), Gas, and Wood.

**FUGACITY** — A thermodynamic function defined in terms of free energy, which serves as a measure of the escaping tendency of a substance from a given phase. It may be regarded as an ideal or corrected pressure. By definition the fugacity of a perfect gas is equal to its pressure ; the fugacity of an actual gas is always lower than its pressure, which in turn is lower than the pressure calculated from the ideal gas laws for the same temperature and molal volume. The fugacity of a liquid may be regarded as a corrected vapour pressure. The ratio of fugacity  $f$  to pressure  $P$  is termed the Activity Coefficient  $\gamma$  ( $\gamma=f/P$ ). In a polyphase system in equilibrium the fugacity of each component is the same in each phase.

Fugacity is of practical interest to the chemical engineer because, if it be substituted for pressure in the Raoult-Dalton equation, the latter can be applied to high-pressure systems with less error than in its original form. This is important, for example, in the design of high-pressure distillation columns. The fugacity form of the Raoult-Dalton equation is :  $f_a = f_\pi \gamma_a = f_\psi \chi_a$ , where  $f_a$  = fugacity of component  $a$  in a vapour-liquid system under the conditions of the system ;  $f_\psi$ ,  $f_\pi$  = fugacity of the pure liquid and vapour  $a$ , respectively, at the temperature ( $T$ ) and pressure ( $\pi$ ) of the system ;  $\chi_a$ ,  $\gamma_a$  = mole fraction of component  $a$  in the liquid and vapour, respectively. The substitution of fugacities for pressures does not make the gas laws or the Raoult-Dalton equation apply exactly to non-ideal systems, and in the critical region there may still be considerable errors.

Fugacities may be calculated from activity coefficients where these are known. Watson and Smith have plotted generalized activity coefficients for gases, derived from the Theorem of Corresponding States (reference below). At pressures well below the critical the activity coefficient of a gas is approximately equal to its Compressibility Factor, therefore fugacities can often be determined with sufficient accuracy from compressibility data. Lewis and Luke give curves of fugacities and compressibility factors of hydrocarbons (reference below). Their fugacities are not always the true thermodynamic functions, but are, in effect, empirically corrected pressures for use with the Raoult-Dalton equation at high pressures.

*References* : G. N. Lewis and M. Randall, *Thermodynamics and Free Energy of Chemical Substances* (McGraw-Hill Book Co., New York) ; W. K. Lewis and C. D. Luke in *Ind. Eng. Chem.*, **25**, 725 (1933) ; K. M. Watson and R. L. Smith in *National Petroleum News*, July 1, 1936.

**FULLER'S EARTH** — A natural porous, absorptive, and colloidal aluminium silicate, containing also some magnesia and a little iron. It is of greyish, yellowish, or greenish colour, and clay-like character, widely distributed and largely produced in England, Saxony, Bohemia, and in the U.S.A. (particularly Florida), constituting a powerful absorbent of oily matters. It is supposed to be derived from the decomposition of hornblende and pyroxene igneous rocks, and is prepared for use by drying, grinding, and sieving to the desired degree. The several varieties differ widely in specific surface, sp. gr. from 1.7 to 2.4 (depending upon the degree of hydration), absorption power, and catalytic activities. At one time it was extensively used for "fulling" clothes, but now it is chiefly employed in clarifying and decolorizing lubricating oils, edible and non-edible oils and fats, hydrogenated shortening compounds, oleomargarine, and some inorganic substances. Both percolation and contact filtration (agitation followed by filtration) methods are used. Organic chemical solvents and dry-cleaning liquids are recovered by both methods. See G. A. Schroter on "Bleaching Clays Find Increasing Use" (*Engineering and Mining Journal*, **140**, No. 11, 35 (November 1939)). Its bleaching action is attributed to a combination of mechanical and electrical properties, the active constituents being probably hydrated silica and hydrated aluminium silicate. The different varieties vary in their power of absorbing the same colouring matter ; one variety often proves capable of bleaching one kind of material, and ineffectual with another.

The English supply of fuller's earth comes chiefly from Surrey quarries and some Somerset mines. An analysis of the Surrey (Nutfield) earth has been given as follows : 58.66 per cent. silica, 17.33 per cent. alumina, 7.21 per cent. ferric oxide, 3.17 per cent. lime, 3.26 per cent. magnesia, 1.63 per cent. soda and potash, and loss on ignition 8.74 per cent. Extensive deposits also occur in Southern Saskatchewan (Canada), and Java, an analysis showing the latter to contain 58.6 per cent. silicic acid, 21.2 per cent. aluminium, and 3.7 per cent. lime. In the U.S.A. the producing states are Georgia, Florida, Texas, and Illinois.

A mixture of fuller's earth and sodium bicarbonate is alleged to be a good application for extinguishing petrol-store fire. (See "Adsol.")

**"FULLERSITE"** — Powder obtained by grinding Welsh slate waste, and used in making artificial stone, flooring material, as a filler, base for paints, oil refining, road construction in admixture with bitumen, etc.

**FULMINATING GOLD** — A compound of auric oxide ( $\text{Au}_2\text{O}_3$ ) and ammonia, of explosive character, the exact chemical constitution of which has not been ascertained.

**FULMINATING MERCURY** (Fulminate of Mercury, Oxycyanide Pyrofulmin) ( $\text{Hg}(\text{CNO})_2$ ) — A crystalline, poisonous compound used for priming percussion caps and in making detonators. It explodes when dry under the slightest friction, and has to be kept wet until used. It is formed as a white precipitate by heating a solution of mercury in excess of nitric acid with alcohol, and is stated to be changed into a non-explosive substance by heating to  $90^\circ \text{C}$ . for about 100 hours either wet or dry. The use of fulminating mercury as a detonating compound has been largely superseded by lead azide. Its structure is discussed by F. H. Van Leent (*B.C.A.*, A, 1931, 181). (See Garner and Hailes on its thermal decomposition and detonation in *Proceedings of the Royal Society*, 139, A, 576 (1933) ; Azides, and Detonators.)

**FULMINATING SILVER** is prepared by dissolving silver oxide ( $\text{Ag}_2\text{O}$ ) in strong ammonia, and is an explosive compound, possibly of the nature of a nitride ( $\text{Ag}_2\text{N}$ ).

**FULMINIC ACID** ( $\text{HCNO}$  or  $\text{C}=\text{NOH}$ ) is the oxime of carbon monoxide. It is known only in the form of its salts, of which the lead and silver compounds are the most important, being used as detonators.

**FUMARIC ACID** ( $\text{COOH}.\text{CH} : \text{CH}.\text{COOH}$ , *trans.*) is a natural constituent of some plants, fungi, and lichens, including *Fumaria officinalis*, *Glaucium flavum*, and Iceland moss, and results from the fermentation of saccharine liquids containing the requisite nutrient materials, such as beer-wort, grape-juice, etc., with a pure culture of *Aspergillus javanicus* (*A. fumaricus*). It crystallizes in colourless prisms, is odourous, has an acid taste, and is readily soluble in hot water, alcohol, and ether. It is allied in constitution to maleic acid, which is the *cis* isomer, and is resolved into succinic acid by the action of reducing agents. Like most *trans* isomers the melting point of fumaric acid ( $287^\circ \text{C}$ .) is higher than the *cis* form ( $130^\circ \text{C}$ . for maleic acid).

**FUMED OAK** is prepared by fumigation of the wood with ammonia, the darkening resulting from the action of that substance in association with atmospheric oxygen.

**FUMIGATION** — Exposure to the action of vapours or fumes, as when fumigating a room by sulphur dioxide generated from a burning sulphur candle, for the purpose of disinfection or for the destruction of bugs and other obnoxious insects, rats, etc.

The vapours of formaldehyde and paraform have identically the same value as germicidal agents when used for fumigation of rooms, and the presence of water vapour does not facilitate the disinfection.

For the fumigation of ships and rat destruction by hydrocyanic acid gas, the U.S.A. Public Health Service recommends a mixture of powdered sodium cyanide 4 ounces, sodium chlorate 3 ounces, talc 2 ounces, commercial hydrochloric acid 17 ounces, and water 34 ounces for each 1,000 cubic feet. The volume percentage used varies from 0.2 to 1.0 ; the time of application about 4 hours, followed by 12 to 18 hours' aeration. The gas may also be generated by the action of atmospheric moisture on calcium cyanide ("Cyanogas"). Fruit and

vegetables are liable to undergo serious damage by excessive fumigation with hydrogen cyanide, and that agent is of doubtful value in controlling the infection of fruits with bacteria and moulds.

Other fumigants which have found considerable application are methyl bromide ( $\text{CH}_3\text{Br}$ ), chloropicrin ( $\text{CCl}_3\text{NO}_2$ ), carbon tetrachloride ( $\text{CCl}_4$ ), carbon disulphide ( $\text{CS}_2$ ), ethylene dichloride ( $\text{C}_2\text{H}_4\text{Cl}_2$ ), and ethylene oxide ( $\text{CH}_2\text{—CH}_2$ ).

Naphthalene and *para*-dichlorobenzene, which are commonly used to protect clothing against insect damage, are also considered as fumigants. (See Martin, *Scientific Principles of Plant Protection* (E. Arnold, London); D. E. H. Frear, *Chemistry of Insecticides and Fungicides* (D. Van Nostrand Co., New York); Insecticides.)

**FUMING SULPHURIC ACID** — See Sulphur.

**FUNGI** — The fungi are generally regarded as an enormously large class of plants of very low order—some 30,000 to 40,000 known species—including moulds, mildews, rusts, toadstools, puff-balls, and some microscopic forms of bacteria. So far as they initiate or take part—as they do—in respect of many chemical changes affecting vegetable life, tobacco, milk, carbohydrates, fats, etc., reference is made to them elsewhere in this work.

Moulds are minute fungi, the common white mould being the so-called *Mucor mucedo*, the bread mould is known as *Aspergillus herbariorum*, and that which grows on jam and fruit as *Penicillium glaucum*. A large number of the spores of fungi are always present in the atmosphere, and, finding suitable pabulum, speedily develop into fungi, notably the spores of *Aspergillus* and *Penicillium*. The “black-spot” of cold-store meat is attributed to the fungus *Cladosporium herbarum*.

Certain moulds have been found to produce substances that arrest the development of bacteria. Of these, penicillin has demonstrated tremendous value in combating certain infections. (See Penicillin.)

Yeasts constitute another division of fungi. Some varieties, for example, *Dermocyste sanguinea*, yield dyes to suitable solvents such as alcohol.

A summary reference to chemical products resulting from the life history of a large number of moulds in a mineralized solution of glucose as made in the Nobel Ardeer Laboratory is given by H. E. Armstrong in *Chem. and Ind.*, **49**, 783 (1930); on “Growth and Nutrition of Fungi,” by E. J. Moore in *Analyst*, **58**, 564 (1933); see also *Fungus World*, by R. T. Rolfe and F. W. Rolfe (Chapman and Hall, Ltd., London); *Moulds, Yeasts, and Actinomycetes*, by A. T. Henrici (Chapman and Hall, London). (See also Decay, Fermentations, Insecticides, Lichens, Mildew, and Yeasts.)

**FUNGICIDE** — A substance which possesses the power of killing or preventing the growth of fungi. Most fungi are non-pathogenic to human beings, but some skin conditions are due to infection with fungal organisms; ringworm of the scalp and of the feet (Athlete’s Foot) is due to such an infection. Various substances have been used

in medicine for the treatment of ringworm, including solutions of iodine, mercury compounds such as phenylmercuric nitrate, salicylanilide, etc. (See "The Treatment of Ringworm of the Scalp" by R. T. Brain, K. Crow, H. Haber, C. McKenny, and J. W. Hadgraft (*Brit. Med. J.*, **1**, 723 (1948)).)

The materials most commonly used to combat fungus diseases of plants include compounds of copper and sulphur (which see). Several organic compounds, including thiuram disulphides, phenols, and quinone derivatives, have considerable use as fungicides. Organic derivatives of mercury ("Semesan," "Ceresan,") are widely used to protect seeds from attack by fungi during germination. (See *Scientific Principles of Plant Protection* by H. Martin (E. Arnold, London); *Chemistry of Insecticides and Fungicides*, by D. E. H. Frear (D. Van Nostrand Co., New York); "Arasan," Copper, "Fermate," Insecticides, "Krenite," "Lignasan," "Milban," "Parzate," Sulphur, "Tersan," and "Zerlate.")

**FUNNELS** — See Filters.

**FUR** — See Hair.

**FURAN (Furfuran)** ( $\text{CH} : \text{CH} : \text{CH} : \text{CH}$ ) is a colourless mobile liquid  
 $\text{[O]}$

with an odour like chloroform, b.p.  $31^{\circ}\text{C}$ ., contained in pine-wood tar, and the products of the distillation of sugar with lime. (See Furfural.)

**FURFURAL (Furol, Furfurol, Furfuraldehyde)** ( $\text{CH} : \text{CH} : \text{CH} : \text{C} : \text{CHO}$ )  
 $\text{[O]}$

when freshly distilled is a colourless, inflammable, volatile, aromatic liquid contained in the products obtained by distilling sugar, wood, or bran with moderately strong sulphuric acid, and can indeed be obtained from straw, oatmeal, jute, certain gums, and any other materials containing pentosans, but oat-hulls and corn-cobs appear to be the best sources, the former yielding some 12 per cent. or more when subjected to the action of steam in rotary digesters, the furfural being recovered from the distillate. The yield being quantitative, the method of production has been used to determine the amounts of pentoses contained in various materials. Air-dried Japanese rice bran is stated to yield from 9 to 10 per cent. Industrial processes by means of hydrolysis, both with and without acids, are in course of development; wood waste and other materials yielding the product when treated with high-pressure steam in the presence of hydrochloric, sulphuric, or sulphurous acids, with or without the use of certain metals or metallic oxides as catalysts.

Furfural turns amber to reddish-brown upon exposure to light and air, has a sp. gr. of 1.159; b.p.,  $161.7^{\circ}\text{C}$ .; f.p.,  $-38.7^{\circ}\text{C}$ .; flash-point, 55 to 57; and ref. ind., 1.5261 at  $16^{\circ}\text{C}$ . It is soluble in water to the extent of 8.3 per cent. at  $20^{\circ}\text{C}$ ., and water is soluble in furfural to the extent of 4.8 per cent. at the same temperature. It is completely miscible with alcohol, ether, acetone, and benzol, but only slightly in the petroleum hydrocarbons. It is an excellent solvent for cellulose

nitrate and acetate ; is used in the lacquer industry and to some extent as a base-dye, several colours being prepared from it by condensation with aromatic amines.

By treatment with amines and phenol, furfural yields a synthetic resin, which is very hard and flexible, and is soluble in "tetralin" ; and this product seems likely to be of considerable service as an electrical insulating material and for other applications.

Furfural can be used as a motor fuel and as a substitute for or in conjunction with formaldehyde in the preparation of synthetic resins and moulding compounds ; also by reason of its germicidal character as a preservative of adhesive pastes and biological specimens, and may find some use as a substitute for turpentine in varnish manufacture, also as a substitute for formaldehyde in tanning.

Some of its derivatives, such as hydrofuramide ("Vulcazol"), furfural, dithiofuroic acid and its salts, are used as rubber accelerators.

*References* : Some fuller details concerning Furoal and its industrial applications by T. H. Barry (*Ind. Chem* , 6, 479 (1930)) ; A. J. Hammer on its use as an industrial raw material and solvent in *Chem. and Ind.*, 52, 608 (1933) ; Fleck, "Furfural and Its Derivatives" (*Plastics*, 11, 534 (1947)) ; and Pectins.

**FURNACES** — Furnaces are widely used in the metallurgical and process industries to bring about physical and chemical changes in materials by subjecting them to high temperatures. There are combustion furnaces and electric furnaces. Combustion furnaces are further subdivided into directly-fired, in which the combustion gases are in contact with the material being heated, and indirectly-fired, in which the material is separated from the combustion gases by a wall through which heat is conducted. In some industries combustion-type furnaces are known as kilns (*e.g.*, lime, cement).

The principal types of process furnaces are as follows :

*Indirectly-fired* : Crucible, Muffle, Tubular Heater.

*Directly-fired* : Open Hearth, Vertical Shaft, Continuous Tunnel, Rotary, Multiple Hearth (with mechanical rabbles).

*Electric* : Arc, Resistance, Induction.

The maximum temperature that can be attained in a furnace depends largely on the properties of the refractory materials used. The actual temperature that a given material will withstand varies with the conditions of load, abrasion, and corrosion effects. The following is a list of common furnace refractories in the approximate order of increasing temperature resistance : fireclay, silica, bauxite, sillimanite, magnesite, zirconia, carbon (in a reducing atmosphere), chromite, carborundum.

Resistor elements in electric resistance furnaces may be made of "Nichrome," carbon, graphite, or silicon carbide.

The output of a rotary kiln may be approximately estimated from the following formula :

$$\text{Tons per day output} = \frac{kLD^2}{100}$$

where  $L$  and  $D$  = length and diameter respectively of kiln in feet ;  $k$  = 1.0 for lime, 1.4 for wet-process cement, 1.6 for dry-process cement.

*References* : W. Trinks, *Industrial Furnaces* (John Wiley and Sons, New York) ; H. Etherington, *Modern Furnace Technology* (Griffin and Co., London) ; J. Griswold, *Fuels, Combustion and Furnaces* (McGraw-Hill Book Co., New York).

**FUSAIN** — See Coal.

**FUSEL OIL** — A by-product in the manufacture of ethyl alcohol by fermentation processes, being produced by the yeast in the metabolic processes. It consists mainly of isoamyl alcohol and *d*-amyl alcohol. It boils chiefly between 128° and 132° C., and has an unpleasant odour and taste, and on account of its objectionable properties it must be removed from the ethyl alcohol. It is used in the preparation of amyl alcohol, lacquers, and varnishes (see Amyl Alcohol).

**FUSES** — See Detonators.

**FUSIBLE METAL** is an alloy, the melting-point of which largely depends upon the proportion of bismuth employed (generally about 50 per cent.), with lead about 20 per cent., tin 12 to 13 per cent., and cadmium about 12 to 13 per cent. One variety has a fusing-point of 67.5° C., and is used for producing casts of metals, solders, in stereotyping, and in making safety-valves for boilers, fusible plugs, valves, etc. (See Alloys, and Bismuth.)

**FUSION** — The liquidation, or melting into the fluid state, of solids by means of heat. The temperatures at which this liquation takes place are called the fusing or melting-points. (See Liquation, Melting-Points, and Metals.)

**FUSION REACTION** — For low mass nuclei the Einstein equation enables us to calculate the energy released in a nuclear reaction by virtue of the decrease in mass. For the fusion of 4  $H^1$  nuclei into 1  $He^4$ , this amounts to 0.7 per cent. of the mass, and of 4  $He^4$  into 1  $O^{16}$  only 0.1 per cent., so only low mass nuclei offer promise. The only known way of accomplishing this type of reaction is by the use of exceedingly high temperature, such as that in the interior of the stars (say 20 million degrees Centigrade) or by the atomic bomb. It has been suggested that the atomic bomb would be necessary to detonate a hydrogen bomb. Even at the high temperature required the average energy of an atom is only 1.7 thousand-electron-volts, which is far below that given to nuclear particles by atom smashers. (See Fission Reaction.)

**FUSTIC EXTRACT** (Cuba Wood) is the name of a yellow dye of two varieties, namely, "old fustic," obtained from yellow Brazil wood (*Morus tinctoria* or *Chlorophora tinctoria*, Gaudich), which is found also in Mexico and the W. Indies and used for dyeing wool mixed shades ; and "young fustic," from *Rhus cotinus*. The colouring matter itself is named *fustin*, and is used in the textile and leather industries. (See Morin, and Sumac.)

**G SALT** — A colour intermediate, being the sodium salt of  $\beta$ -naphthol-6, 8-disulphonic acid.

**GADOLINITE** — A complicated silicate mineral found in Norway and Sweden (known also as yttrite and ytterbyte) of black, brown, and yellow colour, containing beryllium, lanthanum, and the rare earths yttrium, cerium, etc. ; also found in pegmatites in Arizona, Colorado, and Texas (crystal system No. 5, and sp. gr. 4.3).

**GADOLINIUM** (Gd) — Atomic weight, 156.9. See Elements for other data. One of the rare earth elements, and a member of the scandium group of the same. It is found in *samarskite*, *orthite*, *cerite*, etc. The oxide is  $Gd_2O_3$ .

**GAFFA PHOSPHATE** — See Phosphorus, and Sodium (Hydrogen Sulphate).

**GAHNITE (Zinc Spinel)** — A natural zinc aluminate ( $ZnO, Al_2O_3$ ), of crystal system No. 1, and sp. gr. 4.0 to 4.6. (See Zinc.)

**GALACTOSE** ( $C_6H_{12}O_6$ ) — A colourless, crystalline carbohydrate, prepared (1 mole galactose plus 1 mole glucose) by the hydrolysis of lactose with dilute sulphuric acid ; it may also be obtained by hydrolysis of certain gums, known as galactans. M.p.  $168^\circ C$ . Chemically, it is an aldo-hexose like glucose and mannose.

**GALACTOSIDES** — A group of substances, including phrenosin and kersin, occurring in brain-substance, analogous in constitution to the vegetable glucosides, and which yield acids, sphingosine, and galactose upon hydrolysis.

Phrenosin yields phrenosinic acid ( $C_{25}H_{50}O_3$ ), sphingosine ( $C_{17}H_{35}O_2N$ ), and galactose when thus treated, and kersin yields lignoceric acid ( $C_{28}H_{48}O_2$ ), as also sphingosine and galactose.

**GALANGA (East Indian Root)** — The dried rhizome of *Alpinia officinarum* which is cultivated in S.E. China and Hainan. It contains a volatile oil together with an oily substance, galangol, and a tasteless, yellow crystalline compound, galangin (dihydroxyflavanol). (See Flavone.)

**GALBANUM** — See Gums.

**GALENA (Galenite)** — Mineral lead sulphide, of crystal system No. 1, and sp. gr. 7.0 to 7.5. (See Lead.)

**" GALILITH "** — A plastic product or synthetic resin made from casein by hardening with formaldehyde, and used in making buttons and cheap combs, etc. It has a sp. gr. 1.34, a hardness of 2.5, resists acids, oil, alcohol, and benzene, but is attacked by alkalis, and absorbs water when immersed for long periods.

**GALIPOT** — A French name for resin from the *Pinus maritima*. (See Turpentine.)

**GALL (Nuttall, Aleppo Galls)** — The excrescences produced on the leaves and twigs of the oak, *Quercus infectoria*, following the deposition in the tissues of the eggs of the gall wasp, *Cynips gallæ tinctoriæ*. Aleppo galls contain from 50 to 70 per cent. of gallotannic acid and are the most valued. Japanese galls are formed similarly by *Aphis chinensis*

on *Rhus semialata* and contain about 70 per cent. of gallotannic acid. Gall is used in medicine as an astringent, in the tanning industry, for the manufacture of blue-black ink, and for the production of certain tints in Turkey-red dyeing and in calico-printing. (See Myrobalans, Inks, and Tannins.)

**GALLIC ACID (3, 4, 5-Trihydroxybenzoic Acid)** ( $C_6H_2(OH)_3COOH$ ) occurs in catechu, kino, coffee, nut-galls, sumach, tea, and a number of tannins in the form of glucosides from which it can be made by boiling with acids, or by moulds acting on solutions of tannin. In the pure state it crystallizes in nearly colourless silky needles of the composition  $C_7H_6O_5 \cdot H_2O$ , and is soluble in water, ether, and alcohol. With ferrous sulphate it gives a brown colour, which quickly blackens on exposure to the air, and it is used in photography, dyeing, and the manufacture of pyrogallol and ink. A commercial gallic acid is prepared of from 55 to 58 per cent. strength. (See Inks, Tannase, Tannic Acid, and Tannins.)

**GALLIUM (Ga) (Eka-aluminium) and its Compounds** — Atomic weight, 69.72. See Elements for other data. The most important sources of gallium are (1) zinc blende, the richest ores being those mined in Germany, and (2) germanite. Gallium is a grey, lustrous metal with low malleability. It forms many alloys with other metals and combines with chlorine, bromine, and iodine. It is rapidly dissolved in warm hydrochloric and nitric acids (aqua regia). It decomposes water at high temperatures, and its compounds (including the oxide,  $Ga_2O_3$ , and sulphate,  $Ga_2(SO_4)_3 \cdot 18H_2O$ ) resemble those of aluminium. See *Rarer Metals*, by J. De Ment and H. C. Dake (Chemical Publication Co., Brooklyn, N.Y.). Moreover, the unique property of remaining liquid between  $30^\circ C.$  and  $2300^\circ C.$  makes gallium suitable for use in high temperature thermometers above  $500^\circ C.$  (see Thermometers).

**GALL NUTS** are produced as excrescences on the leaves (and their stalks) of the oak (*Quercus infectoria*) by punctures of gall-wasps (*Cynips gallæ tinctoriæ*), in which they lay their eggs. The Aleppo galls are most valued, but although those from the Levant (containing about 60 per cent. tannin) are the best, there are others of inferior quality which come from Dalmatia and other places, including the province of Hunan in China. They contain gallotannic acid or other tannins, some of which compounds are also present in sumach and tea, and are used in tanning, also in the manufacture of blue-black ink, for the production of certain tints in Turkey-red dyeing and in calico-printing. (See also Myrobalans, Inks, and Tannins.)

**GALLOTANNIN** — See Gallic Acid, Tannase, Tannins, and Tannic Acid.

**GALVANIZING** — Coating iron and steel with zinc for corrosion protection. After the material is cleaned (pickled) by immersion in, or scrubbed with, dilute hydrochloric or sulphuric acid so as to remove adherent impurities and to produce a smooth surface, it is fluxed, commonly with sal ammoniac, before immersing into molten zinc. The formation of blow-holes on the metal after pickling is attributed to the absorption of hydrogen from the action of the acid on the metal, and

this action is greater the thinner the sheet (see Bardenheuer and Thanheiser, *B.C.A.*, B, 1929, 818). T. Lewis Bailey and E. Linder have shown that 0.1 per cent. ordinary size (glue) added to the pickling both tends to reduce iron loss and acid consumption. The coating-thickness depends largely on the temperature and viscosity of the bath. Some additions of aluminium (up to 0.63 per cent.) increase the fluidity of the bath. Low temperatures (420° to 450° C.) tend to produce thin coatings. Sometimes 1 per cent. tin is also added, and this results in a zinc coverage of about 500 to 600 grams per square metre. The spangle, or attractive crystalline pattern on the surface of galvanized sheets may be controlled with such eutectic-forming additions as tin, bismuth, cadmium, and lead. Slow cooling is necessary, otherwise the spangle effect may be lost. (See *Galvanizing Handbook*, by J. R. Daesen (Reinhold Publishing Corp., New York).) The coating is a layer of alloy of about 80 to 90 per cent. zinc with iron and has been subjected to X-ray analysis by F. R. Morral and E. P. Miller (*Trans. Am. Soc. Mech. Engrs.*, 143, 158 (1941)). The life of the galvanized sheet depends on the purity of the iron and steel.

Cold galvanizing is carried on commercially by the electrolysis of zinc sulphate solution, using a zinc anode.

About one-half of the total zinc production is estimated as consumed in galvanizing. See also Metals (Calorizing, and Sherardizing).

**GAMBIER** — See Catechu.

**GAMBOGE** — See Gums.

**GAMMA ACID** — Sometimes called Acid G, but also 2-amino-8-naphthol-6-sulphonic acid ( $C_{10}H_5(NH_2)(OH)SO_3H$ ). An intermediate for dyestuffs.

**GAMMA RAY** — Electromagnetic radiation emitted by radioactive materials when certain of these materials disintegrate. (See Nuclear Chemistry, Radioactivity, and Wave Lengths.)

“ **GAMMEXANE** ” (“ 666,” **Benzene Hexachloride**) — A mixture of isomers of hexachlorocyclohexane ( $C_6H_6Cl_6$ ), used as an insecticide. Of the several isomers, only the gamma has been found to possess appreciable toxicity to insects: this is present in the crude reaction mixture to the extent of 10 to 12 per cent. The gamma isomer has a m.p. of 112.5° C., and is insoluble in water, but soluble in a number of organic solvents. It is highly toxic to many species of insects, and may be applied as a dust or spray. The commercial preparations have a strong and penetrating musty odour, which persists for long periods of time: for this reason their usefulness on food plants is somewhat limited, although there are many other applications. (See “ Gammexane,” by R. Slade (*Ind. Chem.*, April, 1945; *Chem. Age*, March 17, 1945); “ Hexachlorocyclohexane as an Insecticide,” by Bourne (*Nature*, 156, 85 (1945)); “ Assay of Toxic Effect of ‘ Gammexane ’ on Man and Animals,” by Taylor and Frodsham (*Nature*, 158, 558 (1946)); “ Chemistry of Benzene Hexachloride and its Insecticidal Properties,” by Chamlin (*J. Chem. Education*, 23, 283 (1946)); *Chemistry of Insecticides and Fungicides* (second ed.), by D. E. H. Frear (D. Van Nostrand Co., New York); and *Insecticides*.)

**GANGUE** — The mineral matter enclosing or intimately associated with metallic and other ores.

**GANISTER** — A highly refractory, close-grained, siliceous, sedimentary rock, found underlying some coal seams; used for making fire-bricks and for lining blast and other furnaces. The mixture generally used consists of the silica mixed with one-tenth its weight of clay. (See Refractories.)

“**GARDINOL**” — A series of proprietary “wettters” used in dyeing fibres. (See Wetting Agents, and Soaps (Sulphated Alcohol).)

**GARJAN OIL (Kenyensi)** — A drying oil available in Burma for use instead of boiled linseed oil in making printing inks, etc.

**GARLIC OIL** — Distilled from *Allium sativum*, a genus of Liliaceæ, comprising garlic, leek, onion, shallot, and chive; is of pale yellowish colour and penetrating odour, containing several allyl sulphides, including  $(C_3H_5)_2S$ . It has a sp. gr. of 1.05, is soluble in alcohol, ether, etc., and is used in medicine and for flavouring.

**GARNET (Carbuncle)** — Name of a variety of cubical minerals (*almandite*, *andratite*, *essonite*, etc.), of crystal system No. 1, and sp. gr. 3.4 to 3.8, of varying colours, consisting of double silicates of various bases, including alumina (many good supplies of which are found in Canada), and utilized to some extent as a wood abrasive. The precious garnet is the variety known as *almandite* or *almandine*  $(6FeO, 3SiO_2 + 2Al_2O_3, 3SiO_2)$ . In some varieties the iron oxide is replaced by lime, manganese oxide, and magnesia respectively, while others contain ferric oxide and chromium as  $Cr_2O_3$  in more or less corresponding combinations. Supplies of different varieties come from Bohemia, Ceylon, Brazil, and Syria (the source of the esteemed Syrian garnets).

**GARNIERITE** — See Nickel.

**GAS (Coal)** — The composition of coal gas as produced for illuminating purposes depends very largely upon the kind of coal used, temperature at which the roasting of the coal takes place, the construction of the retorts, and the amount of air that gains access to the retorts. The temperature ordinarily observed is from 2,000° to 2,200° F. It contains not only permanent gases, but, in addition, considerable quantities of the vapours of volatile hydrocarbons, to which its luminosity when burning is due. The greater proportion consists of hydrogen (about 35 to 50 per cent.), which burns with a practically colourless flame, and marsh gas or methane ( $CH_4$ ) (about 35 to 40 per cent.), which also gives but little light when burned alone. Among the constituents there are proportions of carbon dioxide, carbon monoxide, nitrogen, oxygen, hydrogen sulphide, hydrocyanic acid, and carbon disulphide.

There is a process for removing these two last-named impurities by passing the gas through a solution of sodium polysulphide, which, becoming saturated with ammonia, converts the hydrocyanic acid into ammonium thiocyanate. The carbon disulphide can also be removed by passing the gas over heated nickel, the products being mainly carbon and hydrogen sulphide.

The purification of coal gas from hydrogen sulphide, hitherto accomplished by the use of hydrated ferric oxide, can also be effected by the "Koppers" Company liquid method, which consists of the use of a dilute solution (1 to 3 per cent.) of sodium carbonate and is largely used in America. The hydrogen sulphide is removed from the solution and the sodium carbonate regenerated for use over and over again by blowing air through it in another tower, sulphur being liberated at the same time and subsequently collected and purified. Practically from 90 per cent. to all the hydrocyanic acid contained in the gas is converted into thiocyanate. It is usually preferred to remove some 85 to 90 per cent. in this way, the remaining quantity being taken out in the iron oxide catch boxes.

Type of Coal (Bituminous)	Strongly Caking	Medium Caking	Non-Caking	Medium Caking Blend
CO <sub>2</sub> , H <sub>2</sub> S, etc.	5.4	7.1	11.1	7.2
C <sub>n</sub> H <sub>2n</sub> .. ..	11.5	8.6	9.4	9.6
O <sub>2</sub> .. ..	1.8	1.3	1.7	1.9
CO .. ..	5.0	5.4	7.1	7.1
H <sub>2</sub> .. ..	15.7	16.0	17.6	15.0
C <sub>n</sub> H <sub>2n+2</sub> ..	49.8	52.4	41.8	48.3
N .. ..	10.8	9.2	11.3	10.9
	100.0	100.0	100.0	100.0

According to the Report of the Fuel Research Board for period ended December 31, 1924, in low temperature carbonization about three-quarters of the weight of coal remains as coke, and 1 ton of average coal carbonized at about 600° C. in externally heated retorts produces about 3,000 cubic feet of gas of a calorific value 700 to 1,100 B.Th.U. per cubic foot, the amount being generally equivalent to 30 to 35 therms, or about 10 per cent. of the heat value of the coal, and analyses of gases from typical coals are given in the following table. (See Coal.)

The saturated hydrocarbons consist chiefly of methane. Light spirit for making motor fuel is recovered by scrubbing to extent of about 1½ gallons per ton of coal used.

The trouble caused by the deposition of naphthalene in the mains and services can be obviated by washing the coal gas with creosote oil, which is capable of absorbing about 12 per cent. of that substance, while any water that is present can be and is, generally speaking, removed by the use of solid or liquid absorbent agents.

The illuminating power of coal gas is chiefly attributable to olefiant gas and other associated hydrocarbons (the C<sub>n</sub>H<sub>2n</sub> or olefin type), which, in all, amount to about 5 per cent., and the process of roasting the coal is conducted in such a way as to yield about 10,000 cubic feet of gas per ton of coal.

The composition of good coal gas according to one analysis, which is fairly representative, is as follows

Hydrogen .. .. .	48.2	per cent.
Methane .. .. .	34.2	„
Carbon monoxide .. .. .	6.6	„
Olefines and benzene .. .. .	5.3	„
Nitrogen, carbon dioxide, and oxygen .. .. .	5.7	„
	<hr/> 100.0	

The gas, however, now often supplied consists of a mixture of ordinary coal gas with from 15 to 33½ per cent. of so-called water gas, or carburetted water gas—that is, the mixture of carbon monoxide and hydrogen which is produced by passing steam over red-hot coke.

The effect of using too much water gas is to introduce more carbon monoxide than is desirable, as water gas contains about 42 per cent. of that poisonous compound, and complaints have been made that whereas the old-style coal gas contained only about from 6 to 8 per cent., the newer supplies contain much more (15 to 20 per cent.).

There is a well-known process of converting carbon monoxide into carbon dioxide, which consists of passing the gas over an iron oxide catalyst at a fairly high temperature, so that it can be reduced to less than 1 per cent., the carbon monoxide interacting with the moisture to form carbon dioxide and hydrogen, the carbon dioxide being subsequently washed out. This method is reported to largely increase the percentage of hydrogen. Another process, in which the carbon monoxide reacts with steam and hydrogen, uses a nickel-thoria catalyst, at an elevated temperature, yielding methane and carbon dioxide.

When coal gas is submitted to a pressure of 150 lbs. per square inch, liquid hydrocarbons are produced, which are separable to some extent by fractionation, and one of the fractions can be used as a motor spirit of high volatility and great propellant power, but, apart from its cost, it shows a tendency to resinify.

*References:* "Solvents from the Gas Industry," by C. R. Downs (*Chem. and Ind.*, 51, 28 (1932)); "The Utilization of Gas as a Fuel," by C. A. Masterman (*Chem. and Ind.*, 50, 577 (1931)); Coal, Coke-Ovens, Gas-Producers, Hydrocarbons, Methane, Mond Gas, Producer Gas, and Water Gas.

**GAS (Coke Oven)** — See Coke Ovens.

**GAS (Natural)** — Natural gas is a mixture of hydrocarbons associated with petroleum deposits found in many parts of the world, including Transylvania and the U.S.A. (where it has been utilized for the production of finely divided carbon, ethylene dichloride, "Pentanol," gasoline, and extraction of helium, etc.), and parts of Canada, particularly Alberta and Ontario. It can be carried to distant places by piping, the propane and butane being preferably scrubbed out previously, and used to enrich water gas, or liquefied to form a transportable fuel. A scheme has recently been adopted in Canada for storage of enormous quantities

of natural gas (previously wasted) by adsorption in the depleted sands of districts which have become worked out as economic petroleum-producing areas, the gas being conveyed by pipe-lines. Its uses as a raw material in chemical manufacturing are attracting the attention of industrialists and government investigators (see Fuel (Liquid) for Fischer-Tropsch process).

**GAS (Producer)** — See Producer Gas.

**GAS (Toxic)** — See Gases, and Gassing.

**GAS (Water)** — See Water Gas.

**GAS ABSORPTION** — The removal of soluble constituents from a gas by contact with a liquid solvent.

Gas absorption is nearly always a continuous operation. It may be effected in various ways, *e.g.*, (1) bubbling the gas upwards through a descending column of liquid, (2) spraying the liquid downwards through a rising current of gas, (3) causing gas and liquid to flow counter-current in a packed tower. Of these, method (3) is the most common. Spray towers employing method (2) are occasionally used for absorbing very soluble gases such as ammonia. Method (1) is seldom employed outside the laboratory owing to the power needed to compress large volumes of gas sufficiently to overcome the static head of liquid.

Gas absorption is a mass transfer phenomenon, and the size of tower required for a given duty will depend upon the rate of mass transfer. Theoretically the mass transfer coefficient should be expressed per unit area of gas/liquid interface, but since the interfacial area is unknown it is customary to calculate absorption coefficients per unit volume of contact space (in a packed tower, per unit volume of packing).

The rational design of absorption towers is based upon the "two-film theory," first proposed by Jablczynski and Przemyski in 1912 (*J. Chim. Phys.*, **10**, 271), and independently arrived at by Whitman in 1923. The overall resistance to the passage of soluble constituents from gas to liquid is considered to be the sum of two separate resistances due to (1) the laminar film of gas at the interface, (2) the laminar film of liquid at the interface (see Fluid Dynamics). These two resistances are separately evaluated and combined into an overall coefficient. The driving force across the gas film is the difference between the actual partial pressure of soluble constituent in the gas and the equilibrium pressure in contact with the liquid absorbent; the driving force across the liquid film is the difference between the actual concentration in the liquid and the equilibrium concentration in contact with the gas. The overall coefficient must be stated in terms of one or other driving force alone, so it may be correctly expressed in either of the two ways.

*References* : W. K. Lewis and W. G. Whitman in *Ind. Eng. Chem.*, **16**, 1215 (1924); A. P. Colburn in *Ind. Eng. Chem.*, **22**, 967 (1930); E. G. Scheibel and D. F. Othmer in *Trans. Am. Inst. Chem. Engrs.*, **40**, 611 (1944); and standard works listed under Chemical Engineering. For a discussion of Flooding Velocities, see Packed Towers.

**GAS BURNERS** — See Burners.

**GAS CLEANING** — See Cottrell Precipitating Plant.

**GAS FUEL** — See Fuel, Gas, Gas Producers, Producer Gas, and Water Gas.

**GAS GENERATORS** — There are many forms of laboratory gas generators, ordinary bottles and Woulfe's bottles properly fitted up being used as containers of the necessary materials; also ordinary flasks when it is necessary to employ the agency of heat.

*Kipp's apparatus* is designed for the automatic generation of such gases as hydrogen sulphide (sulphuretted hydrogen), and carbon dioxide. The gases are made by interaction of a solid in one compartment of the apparatus and of a liquid at room temperature. It is made of glass, and consists of sections for containing the acid and the iron sulphide or marble as the case may be respectively.

**GAS LAWS** — The following laws describe the general behaviour of matter in the gaseous state.

I. **Boyle's law** : When a given mass of a gas is maintained at a constant temperature the volume which the gas occupies varies inversely with the pressure applied on the gas :

$$V = \frac{k}{P}, \quad \text{or} \quad V_1 P_1 = V_2 P_2,$$

where  $V$  = volume of gas in any units desired,  $P$  = pressure of gas in any units desired,  $k$  = proportionality constant.

This law can be restated as follows : For a given mass of a gas at constant temperature the product of pressure times volume is constant.

II. **Charles' or Gay-Lussac's law** : When a given mass of a gas is maintained (a) at constant pressure the volume of the gas varies directly with the absolute temperature of the gas (Gay-Lussac, 1808), and (b) at constant volume the pressure of the gas varies directly with the absolute temperature of the gas (Charles, 1784).

$$V = k'T \quad \text{or} \quad \frac{V_1}{T_1} = \frac{V_2}{T_2}, \quad \text{and} \quad P = k''T \quad \text{or} \quad \frac{P_1}{T_1} = \frac{P_2}{T_2}$$

where  $V$  = volume of gas in any units desired,  $P$  = pressure of gas in any units desired,  $T$  = temperature of gas in absolute degrees,  $k$  = proportionality constant.

III. **Dalton's law of partial pressure** : The total pressure exerted by a mixture of gases is equal to the sum of the partial pressures of all the component gases in the mixture. The partial pressure of a gas is the pressure that one component of a gaseous mixture would exert if it alone occupied the same volume as the mixture and at the same temperature. For example, if a mixture of oxygen, hydrogen, and nitrogen gases occupied a volume of one litre at a pressure of one atmosphere at 25° C., the partial pressure of oxygen would be that pressure which the same quantity of oxygen, as existed in the mixture, would exert if it alone occupied one litre at 25° C. In general, the partial pressure of a component of a gaseous mixture is equal to its volume per cent. times the total pressure of the mixture (Dalton, 1807).

IV. **Graham's law** : At constant temperature and pressure the rate

at which two gases will diffuse through an orifice is inversely proportional to the square root of their densities or molecular weights :

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}} = \frac{t_1}{t_2} \quad .$$

where  $r$  = rate of diffusion,  $d$  = density,  $M$  = molecular weight,  $t$  = time.

**V. Avogadro's law :** Equal volumes of all gases at the same conditions of temperature and pressure contain the same number of molecules. If one gram molecular weight of any gas is taken at standard conditions ( $0^\circ \text{C}$ . and 1 atm.) it will occupy 22.4140 litres. The number of molecules assigned to one molecular weight is called Avogadro's number and has a value of  $6.0235 \times 10^{23}$ .

**GAS MANTLES** of incandescent character are prepared from ramie yarn, silk substitutes, and other materials, by impregnation with mixtures of thoria and ceria—the rare earths which are found in monazite sand and some other minerals. After impregnation with the necessary chemicals, the mantles are lightly coated with collodion solution to give strength to the texture. The impregnation is ordinarily effected by soaking the mantles in a solution of thorium and cerium nitrates in the proportion of 99 to 1, other substances being sometimes introduced for specific reasons, for example, beryllium nitrate to increase the hardness of the mantle, after which, and before coating with collodion, they are dried and ignited to burn off the fibre and cause the deposition of the oxides (thoria and ceria) from the nitrates on the ash skeletons of the mantles. The gas mantle at its lowest efficiency renders it possible to obtain fifteen times the light obtainable from any quantity of gas stripped of luminous hydrocarbons. (See Monazite Sand.)

**GAS PRODUCERS** — There are several forms of industrial gas producers (see Producer Gas), but in that form known as the "suction" gas plant anthracite is the fuel that is used, and this is placed in a cylindrical furnace (producer), air and steam being admitted below the burning fuel. The atmospheric oxygen first combines with the burning carbon to form carbon dioxide, and this, in passing through the red-hot mass, is converted into carbon monoxide. The steam is also decomposed, forming more carbon monoxide and hydrogen gas, both of which are combustible, and together with the residual nitrogen of the air constitute a low grade "water gas." This is washed and cooled in a scrubber before being sucked in by the piston of the engine. Coke and peat can be employed in the place of anthracite.

Suction gas made as described has an approximate composition as follows, and a calorific value of about 140 B.T.U. per cubic foot :

Carbon monoxide .. .. .	18.6 per cent.
Hydrogen .. .. .	17.6 ..
Methane .. .. .	1.6 ..
Carbon dioxide .. .. .	7.2 ..
Nitrogen .. .. .	54.4 ..
Oxygen .. .. .	0.6 ..
	<hr/> 100.0

**GAS PRODUCTION FROM HEAVY FUEL OILS** — Heavy bunker oils of sp. gr. 0.95 and upwards are not altogether satisfactory for use in high-compression engines, hence many attempts have been made to convert such oils into producer gases by partial combustion. The yield varies with the specific gravity and calorific value of the oil, a heavy bunker oil only yielding 96 cubic feet of gas per pound of oil and having a fuel value of 160 B.Th.U. per cubic foot of gas; Diesel oil of specific gravity 0.90 yielding 100 cubic feet of gas per pound of oil; and gas oil yielding up to 120 cubic feet of gas per pound of oil. (See Producer Gas, and Water Gas.)

**GAS REACTIONS (Technical)** — From the investigations of J. Hargreaves and F. Hurter it has been concluded that if in a process it is not essential that a definite rate of flow should be observed, it is immaterial whether that flow goes upwards or downwards; but, on the other hand, in cases where a fixed or low speed of gas movement is essential the gas should be led in downwards if regularity in the process be desired, and that it is safer in all cases to do this when the action is exothermic. The principal obstacle to uniformity of working such processes is due to temperature differences; hence the importance of ensuring that any plant should be as uniformly heated as possible. (See *Thermodynamics of Technical Gas Reactions*, by Fritz Haber (Longmans, Green and Co., London); and Gases.)

**GAS SCRUBBERS** — See Gas Washing.

**GAS WASHING** — The quantity of a gas dissolvable by a given volume of a liquid at a constant temperature is proportional to the pressure of the gas. The solvent can absorb the gas until the vapour pressure of the gas in solution equals the partial pressure of that in the gas entering the washing apparatus. The chemical plants known as the "Gay-Lussac tower" and "Glover's tower" are referred to in describing the manufacture of sulphuric acid (see Sulphur). (See Gas Absorption.)

**GASES** — See Matter.

**GASKETS** — Packings for joints. See article by F. C. Thorn (*Ind. Eng. Chem.*, 28, 164 (1936)).

**GASOLINE** — Name used in respect of varieties of hydrocarbon mixtures used for motor fuel, carburetting gases, also as illuminants, solvents, cleansing agents, in paint-mixing, and making rubber cements. It is commonly understood that of any such mixture used as motor spirit, 90 per cent. of the hydrocarbons should boil below 190° C. (374° F.), and all of them below 225° C. (437° F.). In addition to the straight distillates from crude petroleum ranging in density from 50° Bé. to 90° Bé., there is the cracked product obtained from the higher boiling petroleum at a temperature of about 700° F. The manufacture of "cracked gasoline" now exceeds the production of the product yielded by the original distillation of petroleum, while the gases which constitute a by-product (consisting chiefly of unsaturated hydrocarbons of the ethylene series) are used in making "polymerization gasoline," secondary alcohols and other valuable industrial articles. There is also a very volatile gasoline

obtained by condensing the gas from the oil-wells known as "casing-head gasoline," and a number of other varieties of substitutes, including mixtures of benzol, tetralin, and distillates from shale, coal, and peat. "Alcogas" is an American product consisting of about one-third benzol and toluol (mixture), one-third alcohol and ether, and one-third gasoline or other petroleum distillate. (See J. C. Morrell *et al.* on "Stability of Gasoline to Light" (*Ind. Eng. Chem.*, **28**, 122 (1936)); *Aviation Gasoline Manufacture*, by Matthew Van Winkle (McGraw-Hill Book Co., New York); Motor Spirit, Petrol, and Petroleum.)

**GASOMETER** — Apparatus or plant to contain and measure gas.

**GASSING** from chlorine in chemical works may sometimes occur, and when it does is generally caused by the workmen entering the chambers wherein lime has been chlorinated in the manufacture of bleaching-powder, before the gas has been exhausted, and at other times owing to accidental leakages. Workmen exposed to the danger of escaping chlorine or other hazardous gases should always be provided with an efficient gas-mask.

In World War I, gassing attacks were made by means of chlorine cloud produced by the use of liquefied chlorine, and various other substances were used, including cyanogen chloride ( $\text{CNCl}$ ) (a colourless, poisonous liquid, which boils at  $13^\circ\text{C}.$ ), chloropicrin ( $\text{Cl}_3\text{C}\cdot\text{NO}_2$ ), and phosgene (carbonyl chloride) ( $\text{COCl}_2$ ) (which liquefies below  $+8^\circ\text{C}.$ , and yields a gas of very suffocating odour), xylol bromide and benzyl bromide (with which "tear" shells were at first filled), and later, chloromethyl and trichloromethyl chloroformates—highly poisonous bodies.

The so-called "mustard gas" (yperite) was produced by use of the oily, liquid, dichlorodiethyl sulphide ( $(\text{CH}_2\text{Cl}\cdot\text{CH}_2)_2\text{S}$ ) (prepared from ethylene by the action of sulphur monochloride), which, although it does not produce any immediate effect on the eyes, brings about most severe inflammation and intractable blisters later, acute pneumonia, and other serious results, due to its hydrolysis within the eye, leading to the formation of hydrochloric acid in the live cells.

A number of other chemical compounds, including sulphur trioxide, were also employed.

Suitable chemical applications for neutralizing these various poisons were provided as far as possible, being used as respirators. In a paper issued from the United States Bureau of Mines, the conclusion has been drawn that for general use by firemen and otherwise, a respirator consisting of a canister filled with activated charcoal and surrounded with an effective filter for particulate clouds proves of most general utility. The so-called "Universal" gas-mask as developed in the U.S.A. Bureau of Mines at Pittsburgh has a canister of granular absorbents, consisting of activated charcoal for removing organic vapours; a filter of cotton-wool to remove smokes, dusts, and mists; caustic soda fused on pumice-stone to neutralize acid gases; another cotton-wool filter; fused calcium chloride to remove moisture that would inhibit action of the next absorbent; a mixture of the oxides of man-

ganese and copper ("hopcalite"), with, sometimes, silver and cobalt, that catalyses the oxidation of carbon monoxide to carbon dioxide; and, finally, silica gel for adsorbing ammonia.

Breathing appliances to obviate danger by inhalation of deleterious substances may be classified in respect of their employment in chemical works as follows: those designed to purify the air by removing the contaminating impurities by chemical interaction, adsorption, or mechanical removal (filtration), and self-contained oxygen breathing sets to make good any deficiency of oxygen in the atmosphere.

A solution containing sodium sulphide and soap, used in the form of a fine spray, has been found very effective in purifying the air from certain toxic gases, including chloropicrin, chlorine, phosgene, methylchloroformates, acrolein, bromoacetone, cyanogen chloride, and benzyl iodide, bromide, and chloride. Poisonous gases have been used for extermination of obnoxious birds, rodents, and insects; chlorine giving good results against "pocket gophers" and ground squirrels, while sulphur dioxide, hydrocyanic acid gas, and phosgene have proved useful against rats. (See *Chemicals in War*, by A. M. Prentiss (McGraw-Hill Book Co., Inc., New York); *Chemical Warfare*, by A. A. Fries and C. J. West (McGraw-Hill Book Co., Inc., New York); *Noxious Gases and the Principles of Respiration Influencing their Action*, by Y. Henderson and H. W. Haggard (Reinhold Publishing Corp., New York); and Poisons.)

#### IMPORTANT WAR GASES

TABLE SHOWING THE NAME, SYMBOL, AND CLASSIFICATION  
Data arranged by the Editor.

War Gas	Symbol	Classification
Phosgene (Carbonyl chloride)	CG	Casualty agent Lung irritant (Non persistent)
Ethylchlorarsine	ED	Casualty agent Harassing agent Vesicant (Persistent)
Mustard gas (Dichlorodiethyl sulphide)	HS	Casualty agent Harassing agent (Persistent)
Lewisite	M <sub>1</sub>	Casualty agent Harassing agent Vesicant (Persistent; destroyed by water)
Chloracetophenone	CN	Harassing agent Lachrymator (Non-persistent; destroyed by hot aqueous solution of sodium carbonate)

War Gas	Symbol	Classification
Tear gas solution	CNS	Harassing agent Lachrymator (Persistent)
Adamsite (Diphenylamine- chlorarsine)	DM	Harassing agent Irritating smoke (Non-persistent)
White phosphorus	WP	Casualty agent Incendiary agent Screening smoke
Hexachlorethane	HC	Screening smoke
Titanium tetrachloride	FM	Screening smoke
Smoke mixture (Chlorsulphonic acid— sulphur trioxide mixture)	FS	Screening smoke
Diphenylchlorarsine	DA	Irritating smoke Sneezing agent
Chloropicrin	PS	Lachrymator Lung irritant Sneezing agent
Brombenzyl cyanide	CA	Lachrymator (Destroyed by alcoholic solution of sodium hydroxide)
Chlorine	CL	Lung irritant
Crude oil	CO	Incendiary agent

### MAXIMUM SAFE CONCENTRATION OF GASES AND VAPOURS IN AIR

Principal Authority: *United States Bureau of Mines*

Gas or Vapour	Maximum Safe Concentration in Air Per cent.
Carbon dioxide .. ..	2.0-3.0
Hydrogen sulphide .. ..	0.01-0.02
Sulphur dioxide .. ..	0.01
Carbon monoxide .. ..	0.04
Hydrogen chloride .. ..	0.005
Nitrogen dioxide .. ..	0.003
Hydrogen cyanide .. ..	0.002-0.004
Mustard gas .. ..	0.002
Arsine .. ..	0.001
Carbon tetrachloride .. ..	0.001
Chloroform .. ..	0.001
Benzene .. ..	0.0005
Sulphur trioxide .. ..	0.0002
Carbon disulphide .. ..	0.0001

Gas or Vapour	Maximum Safe Concentration in Air Per cent.			
Bromine .. ..	..	..	..	0.0001
Phosgene .. ..	..	..	..	0.0001
Chlorine .. ..	..	..	..	0.0001
Mercury .. ..	..	..	<	0.0001
Iodine .. ..	..	..	..	0.00005–0.0001
Nitrobenzene .. ..	..	..	..	0.00002

**GASTRIC JUICE** excreted from the peptic glands contains 5 per cent. of various saline substances (particularly sodium chloride), 3 per cent. of pepsin, some rennin and a small quantity of acids, including 0.2 to 0.4 per cent. free hydrochloric acid. It has the power of so altering the character of albuminous substances taken as food as to produce assimilable peptones, the product of stomachic digestion being chyme.

**GAULTHERIA OIL (Oil of Wintergreen)** — A colourless or slightly red essential oil of sp. gr. 1.175 to 1.193, ref. ind. 1.535, and b.p. about 218° C., obtained from the *Gaultheria procumbens*, or Canada tea, of the order Ericaceæ, which grows freely in N. America and particularly in New Jersey. It can be obtained from all parts of the plant, has a pleasant odour, and consists mainly (99 per cent.) of methyl salicylate, from which salicylic acid can be prepared. It is soluble in alcohol, ether, chloroform, and carbon disulphide; and used in perfumery, confectionery, and for flavouring, also in medicine for liniments but is largely replaced by synthetic methyl salicylate (see same).

**GAY-LUSSAC TOWER** — See Sulphur (Sulphuric Acid).

**GEDDA (GHEDDA)** — See Waxes.

**GEIGER-MÜLLER COUNTER** — A sensitive instrument used to detect the presence of radioactivity by utilizing an ionization chamber. When radioactive material sends out radiations they ionize the surrounding air (see Nuclear Chemistry). If this ionization occurs in an electrostatic field of the proper voltage to attract the resulting ions the current so produced is a measure of the number of ions produced, which, in turn, is a measure of the radioactivity.

In a Geiger-Müller counter the ionization chamber consists of a wire in the centre of a metal cylinder enclosing a suitable ionizable gas. The wire and the cylinder are maintained at a potential difference of several hundred volts so that the entrance of an ionizing particle produces a momentary flow of current which is amplified and caused to operate a counting dial.

**GEISSLER'S TUBE** — A glass tube filled with a gas under low tension and provided with platinum electrodes, the gas being rendered luminous when an electric current is passed through.

**GELATIN (Gelatine)** — A complex protein obtained from collagen by boiling animal tissues with water, straining the liquid, and evaporating to dryness. Commercially, it may be prepared from bones by boiling them in water acidified with hydrochloric acid which assists in the

separation of the gelatinous constituents from the calcareous parts. The liquid is evaporated at a low temperature and the residue is dried by exposure to air, yielding a crude gelatin which is subsequently purified. It is prepared in "pearl" form as well as in slabs and sheets. In the dry state, it is almost colourless or has a slightly yellow tint. Immersed in cold water, it swells and becomes translucent but does not dissolve; on heating with water, it is peptized. A 1 per cent. solution in hot water forms a gel on cooling.

Gelatins, prepared from different sources, differ slightly in molecular structure and composition but contain approximately 50 per cent. of carbon, 6.5 to 7 per cent. of hydrogen, and 17.5 to 18 per cent. of nitrogen. The molecular weight, determined by osmotic methods on specially purified material, has been stated to be about 40,000. Collagen, from which gelatin is derived, is believed to consist of a molecule of glycine joined by a peptide linkage to a different amino-acid which is itself attached to a molecule of proline, this chain of three amino-acids being repeated many times in the collagen molecule. (See Adrian Albert, *Pharm. J.*, **1**, 45 (1948).)

Gelatin is largely employed as a clarifying agent and in the preparation of jellies, foodstuffs, confectionery, medicinal capsules, photographic emulsions, bacteriological media, and adhesives. Among other purposes, it has been used in the preparation of a special class of paper which is made by impregnation with a solution of gelatin and subsequent immersion in a solution of formaldehyde. In surgery, gelatin has been used in the form of a sponge ("Gelfoam") as a local hæmostatic (see J. W. Fairbairn and T. D. Whittet, *Pharm. J.*, **1**, 149 (1948)). Although gelatin is well utilized as a protein, it is lacking in essential amino-acids and its food value has been much exaggerated. The calorie value is 1,550 per pound (3,410 calories per kilogram). (See Agar, Chondrine, Glue, Proteins, and Size.)

**GELOSE** — See Agar-agar, Algin, and Seaweeds.

**GELS** — See Colloid Chemistry, and Gelatin.

**GELSEMININE** ( $C_{20}H_{22}O_2N_2$ ) — A white, crystalline alkaloid occurring in the rhizomes of *Gelsemium sempervirens* and other plants of the order Loganiaceæ. It is soluble in alcohol, benzene, and chloroform, but only slightly soluble in water: m.p. 178° C. It is highly poisonous. It has mydriatic properties, but its use for this purpose has been abandoned. **Gelseminine** is an amorphous mixture of alkaloids occurring with gelsemine and possesses a greater physiological activity than gelsemine.

**GEMS** — Precious stones, such as the diamond, ruby, topaz, and emerald. Imitations consist of coloured glasses, but the ruby and the sapphire, identical in all respects with the natural gems, are now produced commercially by the fusion of pure alumina. (See Aluminium.) The colour of the ruby and probably that of the sapphire is due to a small content of chromium; the emerald and aquamarine owe their green tint to the presence of ferrous iron, and are varieties of beryls; the amethyst and the garnet owe their colours to ferric iron or manganese, or both.

**GENTIAN** — The dried rhizome and root of *Gentiana lutea*, a genus of Gentianaceæ which grows in Central Europe and Spain. It contains a trisaccharide, gentianose ( $C_{18}H_{32}O_{16}$ ), which on hydrolysis yields fructose and gentiobiose, a reducing disaccharide. In addition, it contains the bitter principles gentiin and gentiamarin, which are glycosidal in character, and a yellow crystalline phenol, gentisin ( $C_{14}H_{10}O_5$ ). An aqueous infusion of gentian is used as a bitter tonic in medicine and veterinary practice. (See Glycosides.)

**GERANIAL** — See Citral.

**GERANIOL** ( $C_9H_{16}CH_2OH$ ) — The alcohol corresponding with citral, is a liquid constituent of a number of essential oils, and is the chief constituent (90 per cent.) of Indian geranium oil, which is used as a substitute for otto of roses. It is possibly the precursor of piperitol and piperitone; boils at about  $228^\circ C.$ , has a sp. gr. of 0.881, ref. ind. about 1.462, and is stereoisomeric with nerol. It is soluble in alcohol and ether, and by oxidation yields citral. (See Citral, and Nerol.)

**GERANIUM OIL** (Oil of Rose Geranium, Oil of Pelargonium) — A pale yellow or greenish essential oil distilled from the leaves of *Pelargonium radula*, *P. capitatum* and *P. odoratissimum* in France, Spain, Algeria, and in other parts of Africa, having geraniol as its chief constituent associated with some esters; soluble in alcohol and ether. Several varieties of the oil are known in commerce.

**French geranium oil** has a sp. gr. of 0.895 to 0.905 at  $15^\circ C.$ ; ref. ind. 1.465 to 1.470 at  $20^\circ C.$ ; opt. rot.  $-7^\circ$  to  $-11^\circ$  at  $20^\circ C.$  The specific gravity of Bourbon oil ranges from 0.888 to 0.896 at  $15^\circ C.$  ref. ind. 1.462 to 1.467 at  $20^\circ C.$ ; opt. rot.  $-8^\circ$  to  $-40^\circ$  at  $20^\circ C.$  whilst Algerian geranium oil has a sp. gr. of 0.894 to 0.904 at  $15^\circ C.$  ref. ind. 1.465 to 1.467 at  $20^\circ C.$ ; opt. rot.  $-7^\circ$  to  $-12^\circ$  at  $20^\circ C.$

**Turkish geranium oil** (Palmarosa oil) or Indian geranium oil, which comes from the East Indies, is distilled from *Cymbopogon martini*, the *motiya* variety of the native Rosha grass, and contains about 70 per cent. of geraniol; sp. gr. 0.885 to 0.895 at  $15^\circ C.$ , opt. rot.  $-2^\circ$  to  $+2^\circ$  at  $20^\circ C.$ ; ref. ind. 1.474 to 1.485 at  $20^\circ C.$  The composition of Caucasian geranium oil differs considerably from that of the Turkish oil.

**Japanese oils**, obtained respectively from *Pelargonium graveolens*, *P. radula*, and *P. denticulatum*, grown near Tokyo, have been reported to have sp. gr. 0.9178, 0.9234, and 0.8860, and total geraniol content as follows: 23.1 per cent., 26.3 per cent., and 63.5 per cent., respectively.

**GERGELIM OIL** — See Sesame Oil.

**"GERMANIN"** — See Suramin.

**GERMANITE** — A South-West African mineral reported to be richer in germanium and gallium (associated with other metals) than any other known mineral. W. F. de Jong gives it the formula  $Cu_3(Fe,Ge)S_4$ .

**GERMANIUM (Ge) (Eka-silicon) and its Compounds**—Atomic weight, 72.60.

See Elements for other data. Germanium is found in the minerals *argyrodite*, *canfieldite*, and *germanite*, and it forms some compounds in which it functions as a metallic element, and some in which it functions as a non-metallic element. It can be extracted from crude zinc oxide and other sources by methods based upon the volatility of germanium tetrachloride, which is obtained by passing chlorine over a strongly heated mixture of the dioxide and carbon. It is of crystalline character, and combines with the alkaline hydroxides, forming compounds corresponding to silicates. Pure germanium manifests an unusual behaviour in electrical conductivity over a wide temperature range, reaching a maximum in resistance at about 165° C. (see C. C. Bidwell, *Phys. Rev.*, **19**, 447 (1922)). It forms alloys with many non-ferrous metals and these possess excellent physical and chemical properties. (See *Rarer Metals*, by J. De Ment and H. C. Dake (Chemical Publishing Co., Brooklyn, N.Y.).)

There are two **oxides**, namely, the dioxide ( $\text{GeO}_2$ ), and the monoxide ( $\text{GeO}$ ), the former being appreciably soluble in water, acids, and alkalis; two **chlorides**, namely, the tetrachloride ( $\text{GeCl}_4$ ), and the dichloride ( $\text{GeCl}_2$ ), the former being a liquid of b.p. 86.5° C. and the latter a white solid; two **sulphides**, namely, the disulphide ( $\text{GeS}_2$ ), and the monosulphide ( $\text{GeS}$ ); and the **hydride** ( $\text{GeH}_4$ ), a gas, of b.p. -90° C.

**GERMAN SILVER** — See Alloys.

**GERMICIDES** — See Antiseptics, and Bacteria.

**"GESAROL"** — Trade name for D.D.T. (see same) insecticide preparations.

**"GESTYL"** — See Gonadotrophin.

**GHATTI GUM** — See Gums and Resins.

**GHEDDA (East Indian Wax)** — See Waxes.

**GHEE** — An Indian clarified butter made from buffalo milk, with or without added cow's, goat's, or sheep's milk, from which moisture, casein, and other constituents have been removed. Its m.p. varies from 34° to 37.3° C., sap. v., from 227 to 238, and Reichert-Wollny value of buffalo ghee from 26 to 41.2 and that of cow ghee from 15.5 to 35.4. It is prepared in Somaliland and India, and is used both in cooking and as a food. For use as a food it is allowed to become rancid, then boiled until all the water is expelled, after which a little dye and salt or betel-leaf is added, then potted for use as required. An imitation "Vegetable Ghee" is made from hydrogenated oils suitably flavoured.

**GILEAD** — See Balsams.

**GILSONITE (Mineral Rubber)** — Utah and Texas deposits of very brittle asphalt of sp. gr. 1.065 to 1.070, soluble in carbon disulphide and hot turpentine; used for making varnishes, waterproofing, lining tanks, and as an insulating material. (See Asphalt.)

**GIN** — The spirit distilled from fermented wort of malted barley and other cereals, and flavoured with the berries of Juniper by distillation. It is the latter which is responsible for any abortifacient properties which the spirit may possess, as Juniper is closely related to the strongly abortifacient savin tops. Gin contains from 51 to 57 per cent. of ethyl alcohol.

“**GINAL**” — A preparation containing sodium alginate used in purification of beet and cane sugar. (See Algin.)

**GINGER** — The dried rhizome of *Zingiber officinale*, a genus of Zingiberaceæ, which grows in India and China and is cultivated in the West Indies, Africa, and Java. Jamaica ginger is the most valued and is prepared by removing the dark outer covering of the rhizome and drying in the sun. It contains up to 3 per cent. of a volatile oil and a pungent oily substance, gingerol, which consists of a mixture of phenolic substances and to which the pungency is due.

**GINGER-GRASS OIL** is distilled from the grass of a species of *Andropogon* (the *sofia* variety of native Rosha grass). It somewhat resembles geranium oil in character, and is used in perfumery. It contains 35 to 70 per cent. geraniol, has a sp. gr. about 0.91 at 15° C., opt. rot. +30° to +54° at 20° C., ester value 10.4, and ref. ind. 1.478 to 1.489 at 20° C. There are, however, a number of varieties from other sources including one obtained from *Cymbopogon martini*. (See Geranium Oil, and Naal Oil.)

**GINGER OIL** — A yellowish, aromatic oil of burning taste obtained by distillation from the dried rhizome of *Zingiber officinale*; soluble in alcohol and ether; sp. gr. about 0.88; opt. rot. -25° to -45° at 20° C.; ref. ind. 1.488 to 1.495 at 20° C. It is used in perfumery, for the preparation of liqueurs, as a flavouring agent, and in medicine as a carminative. It contains phellandrene, together with a sesquiterpene, zingiberene, and a number of other substances including an alcohol, zingiberol (C<sub>15</sub>H<sub>26</sub>O), and zingerone (C<sub>11</sub>H<sub>14</sub>O<sub>3</sub>). (See Ginger.)

**GINGELLY OIL** — See Sesame Oil.

**GINSENG** — The root of *Panax quinquefolium* (order Araliaceæ), containing a saponin, volatile oil, fatty oil, and glucoside. It finds technical uses, and is employed medicinally by the Chinese. Korean and Canton ginsengs are of approximately equal qualities.

“**GIX**” — A German insecticidal preparation developed during World War II. The active principle is 2,2-bis(*p*-fluorophenyl)-1,1,1-trichloroethane, and is thus closely related to D.D.T. (see same).

**GLASS** — Glasses have been defined by C. H. Desch as “undercooled liquids of high viscosity,” and thus distinct from ordinary solids and crystals (see Matter). They are fused mixtures of silicates of potassium or sodium, which alone are soluble in water, with one or more other silicates, which are insoluble in water, such as those of calcium or magnesium. Mediæval window-glass was a potassium-calcium silicate, the alkali being obtained from the ashes of plants, whereas the modern glass is of a sodium-calcium silicate (or soda-lime) character. In

practice, ground quartz or flint or clean sand (free from iron), mixed with potassium or sodium carbonate and the other ingredients, are fritted together in ovens or furnaces of various designs, by which means the silica of the quartz or sand enters into combination with the bases, thus forming glass.

Fire-clay pot furnaces are gradually being superseded by so-called tank furnaces, not only in respect of sheet glass, but for green and blue signal lights, selenium ruby glass, electric light bulbs, etc. The "cyclone tank" is another kind of furnace, by means of which British glass is made much more cheaply than heretofore.

It is of importance that the sand should be of high purity (98 to 100 per cent.  $\text{SiO}_2$ ) and the iron oxide content low. When the iron content is not more than 0.2 per cent. in the sand, the green colour of the glass can be neutralized by some decolourizer, such as manganese, selenium, cobalt, or nickel.

Common glass has a composition approximately represented by the formula  $\text{Na}_2\text{O}, \text{CaO}, 6\text{SiO}_2$ .

There are many and very great varieties of glass, differing from each other in their respective compositions, qualities, and uses. When the mixture used (as for plate-glass making) consists only of sodium carbonate, calcium carbonate, and sand, the two carbonates are first of all fused together, and then at a higher temperature they are decomposed by the silica of the sand, the two bases combining therewith, whilst carbon dioxide is evolved. The greater the proportion of silica, the higher the temperature required for fusion of the mixture. (See "Chemical Analysis of Glass," by G. E. F. Lundell (*Ind. Eng. Chem.*, 25, 853 (1933)).)

Cullet (refuse glass) is largely used in making up glass batches in amounts varying with the types of glass and the method of working, and from experimental work conducted by various research workers, it would appear that, subject to certain conditions, including the maintenance of the chemical composition of the glass by observing the proper heating, the addition of cullet is unobjectionable.

**Window or Soda-Lime Glass** is made by fusion from a mixture of sand, sodium carbonate or sodium sulphate, and lime or limestone of clear good quality, and has a low fusion-point. The usual soda-lime-silica glasses may be regarded as ternary mixtures of  $\text{Na}_2\text{SiO}_3$ ,  $\text{CaSiO}_3$ , and  $\text{SiO}_2$ , the two crystalline silicates being held in solid solution by the excess of silica present in the glass. Some typical analyses show  $\text{SiO}_2$ , 71.9 to 74.3 per cent.;  $\text{CaO} + \text{MgO}$ , 11.1 to 14.2 per cent.;  $\text{Na}_2\text{O}$ , 12.7 to 15.1 per cent.

Varieties of glass are produced which transmit light of wave length less than 3,200 A.U. (in the region of the ultra-violet radiation), to which ordinary window glass is practically opaque.

**Bohemian Glass** is made in considerable quantities at Sazava and elsewhere from pure potassium carbonate and powdered quartz, and is not so fusible as window glass, one type capable of resisting chemical action having the composition:  $\text{SiO}_2$ , 77 per cent.;  $\text{K}_2\text{O}$ , 7.7 per cent.;  $\text{CaO}$ , 10.3 per cent.; and  $\text{Na}_2\text{O}$ , 5 per cent.

Some published analyses (all data in per cent.) of different varieties of glass are as follows :

[illegible]

For chemical apparatus, a soda-lime glass is preferred for the most part, although the potash-lime glass is superior when the articles to be made should be hard or difficult to fuse, as, for instance, glass combustion tubing used in making organic analyses.

Up to the time of World War I, Thuringia and Bohemia enjoyed almost a monopoly of this chemical glass industry; but as a result of investigations conducted by chemists in Britain and the United States during and after the war, working formulas or recipes for a number of qualities for chemical and other scientific purposes were successfully introduced.

Water exercises a corroding effect on glass, some kinds of which, when boiled in water, actually gain in weight.

The tests of good glasses for chemical use include the action of boiling water, boiling water under pressure (autoclave), and the action of salts, acids, and alkalis. The power to withstand sudden changes of temperature is an essential property for chemical glass. A test that has proved satisfactory is to heat a solution of 1 part in 1,000 of the alkaloid narcotine hydrochloride in the vessel to boiling point, and if the glass is of poor quality, the alkaloid is thrown down as a fine precipitate. If this occurs after ten minutes, the glass is to be condemned, and if within twenty minutes, the glass is poor, good glasses not showing any deposit for an hour.

"**Pyrex**" is a variety of laboratory glass highly resistant to water and acids, but not so resistant to alkalis, and is used for baking ware, chemical apparatus, and is competitive with chemical stoneware. It has a smaller coefficient of expansion (0.0000032) than either porcelain or ordinary glass, so that beakers and flasks can be made with thicker walls than usual, thus increasing their durability. The softening point is about 800° C., although it softens slightly under pressure at above 600° C., and is not affected with devitrification in its working range. It contains about 80 per cent. silica and 12 per cent. boron oxide ( $B_2O_3$ ), 4 to 5 per cent. alkaline oxides, and about 2 per cent. alumina, the durability of the glass being at its maximum with this content of the boron oxide. It does not absorb heat by solar radiation to the same extent as porcelain, and has ideal properties for electric insulation.

"**Monax**" is a borosilicate glass of high resistance, which softens at about 720° C., with a coefficient of expansion of 0.0000044, and can be quenched in cold water from 240° C. without breaking. "Chance's resistance glass" is another variety.

**Fused Silica or Quartz Glass** of opaque and transparent characters is now largely used in the construction of chemical apparatus and plant, and for many laboratory operations, as it only melts at about the same high temperature as platinum, and is very resistant to the action of chemicals, except that metals, metallic oxides, and alkalis attack it. Moreover, it is not liable to breakage by sudden changes of temperature.

"**Vitreosil**" — A trade proprietary name for pure fused silica (99.8 per cent.  $SiO_2$ ) used for making laboratory ware of great strength and durability, heat and acid proof; made in opaque, translucent, and transparent varieties, sp. gr. about 2.7; having the low-expansion co-

efficient of 0.00000054, and m.p. between 1,700° and 1,800° C. A clear transparent variety is made.

**Coloured Glass** — To impart colours to glass metallic oxides are frequently used, that of manganese giving a purple tint, cobalt oxide a blue colour, uranium oxide a yellow colour, cuprous oxide a ruby red. Glasses free from heavy metals are coloured yellow by sulphur. To soda-lime glasses selenium gives a yellow to chestnut-brown colour; tellurium can be used to give a purple-red and in some other cases a blue coloration; chromium oxide gives greens or reds; and gold chloride to potash-lead glass a ruby red colour. Both the copper and gold ruby red glasses depend upon the formation of colloidal particles of metal, and to produce this effect it is necessary to carry on a re-heating operation. Selenium is used as a decolorizing agent. (See Selenium.)

Zirconia can be used to some extent to replace silica in glass-making. (See Zirconium.) With respect to the employment of titania in glass-making, see Titanium.

**Safety (Laminated) Glass** — Varieties of this character, designed to decrease splintering under impact, depend upon the employment of a tough material between two hard and relatively brittle sheets of plate glass. Such substances as cellulose acetate, or celluloid in the form of thin sheets, are used between the glass plates. (See "Safety Glass," by J. Wilson (*Journal of the Society of Glass Technologists*, 16, 67 T (1932)); and "Butacite.")

**Fibrous Glass** — The mechanical development of fibre glass is described by J. H. Plummer in *Ind. Eng. Chem.*, 30, 726 (1938). Such glass serves as a heat-insulating material, is fire-proof and vermin-proof. It is also woven into fabric.

**Fritted Glass** bottoms of glass filtering crucibles have proved a welcome innovation. Various degrees of porosity are made; no filter paper is required; and cleaning is done by heating.

**Glass Enamels** (Du Pont) are finely ground glass of melting points between 540° and 600° C. (1,004° and 1,112° F.), and pigmented for partial or total coating of glassware.

**Actinic Glass** — Crookes used cerium salts, also biotite, as ingredients to produce glass which would prevent the passage of heat rays and certain deleterious light rays, in order to protect the eyes of labourers engaged in glass-works. This so-called "actinic glass" is now made commercially in forms of "plate," "wire," "aqueduct," "corrugated wire," etc., the "aqueduct" quality being used for roofing, skylights, etc. The following composition of a batch for such glasses is published: Sand 1,300 pounds, soda ash 400 pounds, borax 20 pounds, lime 200 pounds, nitre 40 pounds, manganese dioxide 85 grms., titanium oxide 30 grms., nickel oxide 35 grms., artificial biotite 40 pounds; whilst that of the artificial biotite is given as consisting of micaceous hæmatite 40 pounds, precipitated alumina 5 pounds, solid sodium silicate 50 pounds, magnesite 5 pounds, manganese dioxide 30 grms., all finely ground and thoroughly mixed before addition to the batch, the whole being fused together at 1,100° C.

With respect to ultra-violet light-transmitting glasses, Starkie and Turner determined some as follows: "Sanalux" 73 per cent., "Sun Ray" 62 per cent., "Holvi" 61 per cent., "Vita" 54 per cent., "Helio" 52 per cent., "Uviol" 46 per cent., while "Corex," having the lowest iron oxide content, transmitted practically as much light as quartz (89 per cent.), although the other glasses were more durable upon exposure.

**Opal Glass** — Opacification of glass results from the colloidal separation of materials added for the purpose, aluminium compounds being often used in association with fluorides and fluorosilicates. Barium carbonate, cryolite, sodium silicofluoride, and sodium fluoride are approximately equally effective as opalizers, while sulphates, chlorides, phosphates, and tin oxide are also used. Zirconium is used in the production of clouded opal glass, while neodymium and praseodymium are also employed in making certain other special glasses, and on account of their allochroism for making artificial gems. On account of the physical and tinting characters imparted to glass, the use of the rarer metals is rapidly increasing.

**Devitrification** is the loss of transparency or vitreous character by crystallization, and is most commonly due to separation of silica. This occurs more readily in glasses containing lead oxide than in those containing the same proportion of calcium oxide. With sheet (window) glass the danger temperature region is from 700° to 800° C., and the addition of alumina raises this about 100° C.

**Polishing of Glass** — Preparations used for polishing glass include rouge (ferric oxide), "Glassite" (containing the black oxide of iron as its principal constituent), fine "Carborundum" (silicon carbide) after treatment with hydrofluoric acid and using oil as a medium, and carbon prepared in a suitable physical condition for use as an abrasive. (See also Enamels.)

*References:* G. W. Morey on the  $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$  System (*Ind. Eng. Chem.*, **25**, 742 (1933)); D. E. Sharp on "The Chemical Composition of Commercial Glasses" (*Ind. Eng. Chem.*, **25**, 755 (1933)); "Glass-Lined Steel Equipment," by P. S. Barnes (*Ind. Eng. Chem.*, **29**, 378 (1937)); *A Bibliography of Glass*, by G. S. Duncan (H. F. and G. Witherby, High Holborn, London); *Notes on the Analysis of Glasses, etc.*, by W. E. Turner (Society of Glass Technology, Sheffield); *A Textbook of Glass Technology*, by F. W. Hodkin and A. Oousen (Constable and Co., London); a series of papers on the "Constitution of Glass," edited by W. E. Turner (Society of Glass Technology); *Defects in Glass*, by C. J. Peddle (Glass Publications, Ltd., London); *Properties of Glass*, by G. W. Morey (Rheinhold Publishing Corp., New York); *Annual Reports of the Progress of Applied Chemistry* (Society of Chemical Industry).

**GLASS-BLOWING** is an art that can only be acquired by practice. Suppose it is desired to make a sealed tube with a bulb at one end: a piece of glass tube of the desired size and length—say  $\frac{1}{8}$  inch diameter and

4 or 5 inches long—is taken, and one end placed in a Bunsen or blow-pipe flame until the glass softens sufficiently to mass together, and becomes solid to the extent of about  $\frac{1}{8}$  inch; the mouth should then be applied to the open end, turning the tube round in the fingers meanwhile and blowing with enough pressure to swell out the molten glass until a bulb of the right size and shape is obtained.

Bulb-tubes thus prepared are useful for observing the behaviour of solid chemical substances placed in them for that purpose when heat is applied. The conveyance to the bulb-tube of the substance to be examined can be easily effected by the use of a sharply channelled slip of paper. Used in this way iodine will be seen to volatilize, give off fumes of its own colour, and to recondense to the solid state in the upper (cooler) part of the tube; sulphur can be seen to melt and pass through the stages described under that heading, including sublimation and recondensation; mercury can be sublimed and seen to condense on the upper cool part of the tube; so also ammonium chloride; lead filings can be melted in the bulb, while white lead is decomposed, carbon dioxide being given off as gas, and yellow litharge being left behind.

Glass T-pieces can be made with a little practice, and are often wanted in the laboratory. Take a piece of glass tube of the desired length, and plug one end with a small boring of cork; then hold it in the flame of a blow-pipe so that a fine tongue of flame impinges upon and heats the tube in one spot only, near the middle; and when it is observed to be red-hot, remove the tube from the flame and place the open end quickly in the mouth. Upon blowing, the molten part will become distended into balloon form, so thin that it can easily be broken, thus leaving a hole in the tube the edges of which can be rounded off with a file. Next, take another piece of glass tube and blow a bulb at one end as previously described, taking care, however, in this case, to blow the bulb as large, and therefore as thin, as possible. This bulb is then to be broken and the edges rounded off as in the other case with a file, when it remains to join the two pieces together. We have then the one tube with a hole in its side, and the other with one end provided with a sort of lip or flange roughly fitting the hole as to size. The flame of the blow-pipe should now be applied to both these parts as held together, and when sufficiently softened by heat they can be joined (welded) in the flame.

**GLASS (LABORATORY) MARKING** — Morkert and Hatfield use a 30 per cent. sodium silicate in water solution, and a steel pen. Another ink recommended for glass is a coloured solution of shellac.

**GLAUBERITE** — A crystalline native double sulphate of sodium and calcium ( $\text{Na}_2\text{Ca}(\text{SO}_4)_2$ ), of crystal system No. 5, and sp. gr. 2.7, occurring in New Castile, Arizona, New Mexico, Bavaria, at Vic (France), and at Tarapaca in Peru.

**GLAUBER'S SALTS** ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) — See Sodium (Sulphate).

**GLAUCONITE (Greensand)** — A compound mineral silicate containing some potash, employed for water-softening.

**GLAZES** — Fusible mixtures used in the ceramic industries. (See Enamels, Glass, Porcelain, and Refractories.)

**GLIADINS** — Cereal proteins soluble in 80 per cent. alcohol and insoluble in water, such as in gluten of wheat and hordein of barley. (See *Advances in Protein Chemistry* (Academic Press, New York, 1944).)

**GLOBULINS** — A class of proteins insoluble in water, coagulated by heating, soluble in dilute solution of salts such as NaCl or  $\text{MgSO}_4$ , including serum globulin of blood, and edestin of hemp seed. (See Albumins, and Proteins.)

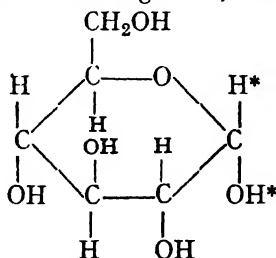
**GLOVER'S TOWER** — See Sulphuric Acid.

**GLUCINUM (Gl)** — See Beryllium.

**GLUCONIC ACID** ( $\text{CH}_2\text{OH}(\text{CHOH})_4\text{COOH}$ ) is made industrially from glucose by the action of the mould *Penicillium luteum purpurogenum*, and is used in baking powders. See O. E. May *et al.* on "Gluconic Acid" (*Ind. Eng. Chem.*, **26**, 575 (1934)); Wells *et al.* on "Gluconic Acid Production" (*Ind. Eng. Chem.*, **29**, 653 (1937)); Moyer *et al.*, "Gluconic Acid Production" (*Ind. Eng. Chem.*, **29**, 777 (1937)); and Glucose.

**GLUCOSANS (Glucosanes)** — Polysaccharoses which, upon hydrolysis yield hexoses. (See Glucose.)

**GLUCOSE (Dextrose)** — There are a number of sugar-like bodies termed glucoses, the best-known member being grape sugar, or dextrose ( $\text{C}_6\text{H}_{12}\text{O}_6, \text{H}_2\text{O}$ ), which is crystalline, soluble in water, and melts at  $86^\circ \text{C}$ . Glucose and sugars of the hexose and pentose types are regarded as being built up in the form of a six-atom ring which can be represented as a hexagon (Haworth), in which ring are five of the six carbon atoms and one of the six oxygen atoms of glucose, thus :



where the formula is that of *alpha*-glucose, and when the marked groups,  $\text{H}^*$  and  $\text{OH}^*$ , are reversed in this formula it is then that of *beta*-glucose. It is believed that only 0.25 per cent. of the molecules possess a *free*

aldehyde group,  $\text{—C} \begin{array}{l} \text{H} \\ \text{=O} \end{array}$ . Experimentally this is supported by the

negative result obtained with Schiff's reagent, and with sodium hydrogen sulphite, which reactions are both positive in the case of aldehydes.

Glucose is contained in honey and in most sweet fruits, and can be prepared from sucrose (cane sugar) or starch by hydrolysis with dilute

acids or enzymes. In its pure form glucose is a white, crystalline substance, to which the name dextrose is usually applied, the term "glucose" being reserved for the more or less pure commercial products, which may be solids or viscous liquids ("liquid glucose"). Dextrose occurs either as the anhydrous variety, D. (+) glucopyranose, or as the less hygroscopic monohydrate,  $C_6H_{12}O_6 \cdot H_2O$ .

Commercial glucose is chiefly made by the more or less prolonged action of dilute hydrochloric or sulphuric acid under pressure upon maize or other starch, and is stated to be a mixture of glucose with varying proportions of dextrin and maltose. When sulphuric acid is used it is subsequently removed by chemical means and the syrup evaporated in vacuum pans until semi-solid, after which it can be run into moulds, constituting, when cold, a hard opaque substance, white or slightly yellow in colour.

There are three grades of the commercial product—viz., liquid, solid, and crystalline. The liquid form of specific gravity about 1.430 containing 14 to 18 per cent. water is really the incompletely hydrolysed product of the same process that yields the other two forms; that is to say, the process is arrested at an earlier stage. The solid product is obtained by a continuation of the process until the dextrin content is reduced to 5 per cent., followed by neutralization of the liquor, then continued concentration to a specific gravity of 1.5, and cooling in moulds. The crystalline variety (one form of which is known as "Ceralose") is much less sweet than sucrose (about 65 per cent.), and is prepared by the same general process. The manufacture of commercial glucose (dextrose) is described in detail in *Starch: its Chemistry, Technology, and Uses*, by Eynon and Lane (Heffer and Sons, Cambridge).

In all three forms glucose is largely used by brewers and others in the manufacture of alcohol and various fermentative processes, also in making jams, confectionery, syrup, vinegar, wines, caramel, and in the paper, textile, and leather trades.

The solid variety sometimes contains up to 50 per cent. or more of inverted products (chiefly gentiobiose—a reducing disaccharose—which is not fermented by yeast) other than glucose.

Dry sawdust or cheap firewood treated with very strong hydrochloric acid results in the conversion of the cellulose content into sugars, mostly glucose (about 65 per cent.), but the operation necessitates the use of "Prodorite" or stoneware vessels. In Switzerland the acid is recovered by introducing hot oil into the resulting product, the acid being evaporated and condensed while the remaining mixture is separated into syrup and oil in a centrifugal machine. (See Sugar.) Wood waste is subjected to a process ("Kocher's") of treatment with hydrogen chloride under pressure, whereby glucose 80 per cent. fermentable is obtained, with the production of 65 to 70 gallons of ethyl alcohol per ton of sawdust. (See Alcohols.)

When cane sugar is hydrolysed by acid treatment it is converted into so-called "invert sugar"—that is, an equal molecular mixture of glucose with fructose.

When glucose is heated to 150° to 155° C. under reduced pressure, it loses water and is converted into the anhydride glucosan ( $C_6H_{10}O_5$ ), which can be obtained in a deliquescent crystalline form, melting at 108° to 109° C., and, when heated with water, is retransformed into glucose. It has been shown by Irvine that when glucosan is fused with a trace of certain metallic chlorides it becomes opaque and passes into a white amorphous substance which resembles starch. When heated to 198° C., glucose is converted into caramel. By oxidation with bromine water, glucose yields gluconic acid (see same); this acid is also produced by the growth of the mould *Aspergillus niger* in nutrient sucrose solutions, and its use has been suggested to take the place of vegetable acids for many commercial purposes. Its manufacture by fermentation of dextrose solutions, using a strain of *Penicillium luteum purpurogenum*, has been successfully demonstrated.

By heating cotton cellulose in a distilling apparatus under the reduced pressure of 10 to 15 mm. it decomposes at 210° C., and an oil of composition represented by  $C_6H_{10}O_5$ , supposed to be the anhydride named lævo-glucosan, equal in weight to 45 per cent. of the cellulose distils over and subsequently solidifies. It has been proved that crystalline glucose (m.p. 145° C.) can be obtained from normal cotton cellulose to the extent of 90 per cent. of the theoretical amount. (See W. B. Newkirk on "Development and Production of Anhydrous Dextrose" (*Ind. Eng. Chem.*, **28**, 760 (1936); *An Introduction to the Chemistry of Carbohydrates*, by Honeyman (Clarendon Press, Oxford, 1948); *The Chemistry of the Monosaccharides and of the Polysaccharides*, by Hans Pringsheim (Cornell University Press, Ithaca); *Carbohydrates, Dextrose, Gluconic Acid, Invertase, Lævulose, Manioc, and Sugar.*)

**GLUCOSIDES** — The old name for glycosides, originating from the belief that all glycosides yielded glucose as one of the products of hydrolysis, whereas many of them are now known that yield other sugars instead of, or as well as, glucose. The name glucoside should only be used where glucose is the sole sugar obtained on hydrolysis. Most glucosides are hydrolysed by emulsion, but are usually accompanied in the plant tissues containing them by enzymes which are also capable of effecting their hydrolysis. (See *An Introduction to the Chemistry of Carbohydrates*, by Honeyman (Clarendon Press, Oxford); *Glucosides*, by E. F. and K. F. Armstrong (Longmans, Green and Co., London); *Enzymes, and Rhamnosides.*)

**GLUES** — There are many brands, including so-called "size," all being hydrolytic derivatives of the nitrogenous tissue substances, mainly consisting of glutin associated with small amounts of chondrin and mucin. Ordinary glue is a degraded form of gelatine made from bones, the paring of hides, the pith of horns, and other animal offal, such as tannery waste, by boiling with water and pouring the liquid (after concentration) into frames or moulds, in which it sets to a solid mass. Fish glue is made from the bony structures of the heads of fishes, and is largely used for making adhesives, in finishing textiles, as an addition

to certain rubber goods, and in the felt-hat trade, etc. A good variety of glue can now be prepared from chrome leather waste. (See Tanning.)

A good glue should not attract moisture, and should be capable of absorbing six to seven times its own weight of water without liquefying. The final test of a glue is the tensile strength of a joint prepared from it.

Liquid glue is made by treating ordinary glue with acetic or hydrochloric acid, when it loses its gelatinizing property, but retains its adhesiveness. Glues can also be liquefied by the action of enzymes, but with some loss of adhesiveness. The properties desirable in liquid glue depend upon the intended use, but the gelatine and gelatose content should be high and the gelatine and aminoacid content should be low, high viscosity, low moisture, and neutrality being desirable features.

Glue is generally marketed in slab or sheet form by drying the solidified jelly, but it is now also produced by a patented process in pearls or solidified drops by forcing the glue extract through fine orifices into a liquid or gaseous medium. These droplets measure about 1 mm., are easily dried, and owing to the greater surface they present, a given quantity will take up water in much less time than when prepared in the older forms; moreover, the glue is more readily dried when prepared in this form than are the slabs.

Animal glue can be made insoluble by treatment with formaldehyde, but for the preparation of a water-resistant product it is preferable to employ finely divided paraform and oxalic acid in the proportions of 10 and 5 per cent. respectively on the weight of the dry glue used. The glue is soaked in a suitable quantity of water and then "melted," the mixture then added, and when the oxalic acid has dissolved, the glue is ready for use, and will remain so for some seven to nine hours at not exceeding 45° C. Thymol, beta-naphthol, and orthophenylphenol, the sodium salt of which has a high co-efficiency in respect of mould and putrefactive agents and is readily soluble in water, are among the substances used for the preservation of glue.

*References:* *Glues and Glue Testing*, by S. Rideal (Scott, Greenwood and Son, London); *Glue and Gelatine*, by P. I. Smith (Sir Isaac Pitman and Sons, Ltd., London); *Adhesives, Bones, Gelatine, and Isinglass*.

**GLUTAMIC ACID (Alpha-Aminoglutaric Acid)** ( $\text{COOH} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2$ ,  $\text{CH}_2 \cdot \text{COOH}$ ) — Occurs naturally in beetroot and in the sugar-beet, which is its main commercial source, as well as various other plants. It may also be produced by the hydrolysis of gluten with concentrated hydrochloric acid, with a yield of about 3 per cent. This acid and glutamine correspond with aspartic acid and asparagine. The sodium salt is used in China and Japan as a condiment and is produced industrially in the U.S.A. for the same purpose.

**GLUTATHIONE** ( $\text{C}_{10}\text{H}_{17}\text{O}_6\text{N}_3\text{S}$ ) — A tripeptide, discovered by Hopkins, occurring in most plant and animal tissues. Pure glutathione is a white, crystalline substance, m.p. 190–2° C., named glutamylcysteylglycine, yielding glycine, glutamic acid and cysteine on acid hydrolysis. It is of great importance in the oxidation-reduction regulatory system of the human body. (See Kleiner, *Human Biochemistry* (Kimpton).)

**GLUTEINS** — Vegetable proteins soluble in alkalis and allied to globulins.

**GLUTEN** or **VEGETABLE ALBUMEN** — The albuminoid or protein part of wheat flour, amounting to from 10 to 15 per cent. in the best qualities, and in inferior grades to from 8 to 9 per cent. It is that part of the flour which, when made into a paste and washed with water, constitutes the tenacious part as distinct from that portion which dissolves in the water and the starch portion which goes into suspension in the water. It is soluble in alkalis and in strong acetic acid. Crude gluten may contain from 5 to nearly 20 per cent. of starch content as a filler. The lipid content ranges from 5 to more than 10 per cent., and the ash varies widely. A soft red winter-wheat flour gluten contained 84.5 per cent. of protein, 47.5 per cent. of lipoids, 15.6 per cent. of ash, and 20.4 per cent. total phosphoric acid calculated on the original weight of the flour.

**GLYCERIA WAX** — See Waxes.

**GLYCERIC ACID** ( $\text{CH}_2\text{OH}.\text{CHOH}.\text{COOH}$ ) — A viscid liquid resulting from the oxidation of glycerol (glycerine) by nitric acid; it enters into combination with the alkalis and other bases, forming salts known as glycerates.

**GLYCERIDES** — Esters in which the glyceryl constitutes the alcohol radical, as in triacetin,  $\text{C}_3\text{H}_5(\text{OOC}.\text{CH}_3)$ ; tristearin,  $\text{C}_3\text{H}_5(\text{OOC}.\text{C}_{17}\text{H}_{35})_3$ ; distearin,  $\text{C}_3\text{H}_5(\text{OOC}.\text{C}_{17}\text{H}_{35})_2\text{OH}$ ; diacetin,  $\text{C}_3\text{H}_5(\text{OOC}.\text{CH}_3)_2\text{OH}$ ; diformin,  $\text{C}_3\text{H}_5(\text{OOC}.\text{H})_2\text{OH}$ . The triglycerides occur in fats and oils, and mixed glycerides contain two or three different acid residues in each molecule. An approximately theoretical yield of glycerides can be obtained by heating a mixture of glycerol and fatty acids at a moderate temperature under reduced pressure (Belucci and Manzetti). (See Hilditch, *Industrial Fats and Waxes* (Baillière, Tindall and Cox, London); and Oils.)

**GLYCEROL (Glycerine)** ( $\text{CH}_2\text{OH}.\text{CHOH}.\text{CH}_2\text{OH}$ ) — A syrupy, colourless, and odourless liquid of a somewhat sweet taste, and sp. gr. 1.26. It is soluble in water and alcohol, solidifies to a crystalline condition when exposed to a sufficiently low temperature, m.p.  $17.9^\circ\text{C}$ ., and b.p.  $290^\circ\text{C}$ . At  $70^\circ\text{C}$ . the liquid has a specific heat of 0.5537, and that of the crystalline solid is 0.3778. It is chemically described as a trihydric alcohol and is a product of the saponification of fats and oils. The alkali used for soap-making combines with the fatty acids to make soaps, while the glycerol passes into solution and is recovered from the lye, which contains about 5 per cent.,  $12\frac{1}{2}$  per cent. salt, and some impurities. After concentration of the lyes to about 80 per cent. strength of glycerol and removal of the salt, distillation in steam at  $190^\circ\text{C}$ . gives weak glycerine or so-called "sweet waters," and this, after decolorization by carbon, is reconcentrated *in vacuo* to a sp. gr. of 1.262, or over 98 per cent., and used in the making of high explosives, such as dynamite; it is also marketed in crude form of 80 per cent. strength.

It is also produced by subjecting fats to the action of superheated steam, by which process they are hydrolysed, the glycerine passing

over with the steam, leaving the fatty acids behind ; or the fats can be hydrolysed by heating in water to which a small quantity of sulphuric acid has been added, with or without the addition of catalytic agents. (See Fats (Twitchell Process).) In such case, the fatty acids rise and float on the top of the liquid which contains the glycerol, and from which it can be easily recovered.

The latest development in the concentration of glycerol from the crude product, without the use of free steam, consists in passing the crude article at  $180^{\circ}\text{C}$ . in an atomized state by means of suitable jets into a vessel of higher vacuum, steam coils being used to maintain the temperature at about  $180^{\circ}\text{C}$ . with the aid of condensers and pumps as required.

The various commercial products are known as "chemically pure," "dynamite," "industrial white," and "pale straw" glycerines. The crude material often contains trimethylene glycol ( $\text{CH}_2\text{OH}.\text{CH}_2.\text{CH}_2\text{OH}$ ), from 1 to 3 per cent., and even up to 10 per cent. at times, being the product of a *Schizomycetes* fermentation process. It boils at  $214^{\circ}\text{C}$ ., has a sp. gr. of 1.0602, and resembles glycerol in its physical properties, although it is less viscous. It can be separated from glycerol by fractional distillation, and, being hygroscopic, may be used in its place as a moisture-absorbing material, and in aqueous solution for the prevention of water freezing.

Glycerol has been obtained to some considerable extent in Germany and more recently in the U.S.A., from molasses and sugar by a process of fermentation with a selected yeast (*S. ellipsoideus*) in an alkaline medium. Commercial sucrose, dextrose, lævulose, or invert sugar can be fermented with yeast in the presence of one or more inorganic or organic substances of alkaline reaction, such as disodium phosphate, sodium or ammonium carbonate, or sodium bicarbonate, with or without catalysts such as manganese or iron sulphate. The fermentation is preferably conducted in the presence of sodium sulphite, together with a small quantity of a hydrosulphite or sulphonylate, and the yeast (previously cultured saké and wine yeasts being preferred) can be regenerated by a purifying fermentation in presence of dilute acid and used over again, together with a surplus yield, which can be employed for baking or fodder. In this way the yield of glycerol amounts to from 35 to 40 per cent. of the sugar. One molecule of sugar should yield one molecule of glycerol and no alcohol when the fermentation is conducted in the presence of sodium bisulphite, which fixes the acetaldehyde ; otherwise, two molecules of sugar yield one of glycerol and one of alcohol.

Glycerol is prepared synthetically and commercially from petroleum gases. Pure propylene ( $\text{CH}_3.\text{CH}:\text{CH}_2$ ) is first obtained, and then converted by chlorine to allyl chloride ( $\text{CH}_2\text{Cl}.\text{CH}:\text{CH}_2$ ). This substitution reaction—rather than the usual one of addition—is accomplished by the proper control of temperature, pressure, and concentration of reactants. The allyl chloride is purified, and subjected to treatment with chlorine to convert to 1,2,3-trichloropropane, which is hydrolysed by sodium hydroxide solution to 1,2,3-trihydroxypropane

(glycerol). Water is evaporated from the dilute solution, and the resulting sodium chloride-glycerol slurry is further evaporated in a high vacuum, whereby the glycerol is vaporized and condensed pure. (See *Chem. and Met. Eng.*, Dec., 1940, 834; Jan., 1941, 87; *Chem. Eng.*, Sept., 1948, 96.)

Glycerol is largely used in the manufacture of nitroglycerine and other explosives; in the preparation of perfumes, cosmetics, printing-ink rollers, lacquer solvents, liqueurs, fruit preservatives, blacking, synthetic resins; as a substitute for sugar in preparing marmalade and other food for diabetic subjects; as an "anti-freeze"; for dehydration of coal gas, etc.; when mixed with 5 or 6 parts water as a lotion for chapped and sunburnt skins; for the quenching of steel; and for phthalic anhydride-glycerol resins (see "Glyptal"). Glycerol does not freeze at atmospheric temperatures, and is sometimes used, therefore, as a lubricant for delicate machinery. Although it can be distilled *in vacuo* or in the presence of steam without decomposition, it undergoes decomposition when heated in the air.

*References:* "Glycerol, Liberation, Recovery, and Refining," by A. Guillaudeu (*Ind. Eng. Chem.*, **29**, 729 (1937)); "New Applications of Glycerine," by Georgia Leffingwell and M. A. Lesser (*Chemical Industries*, **42**, 395 (1938)); and *Glycerol and the Glycols*, by J. W. Lawrie (Reinhold Publishing Corp., New York).

**GLYCEROPHOSPHORIC ACID** ( $C_3H_5(OH)_2H_2PO_4$ ) — The monoglyceryl dihydrogen ester of phosphoric acid; a liquid, cleavage product of various substances, such as lecithin, contained in the yolk of egg and brain-matter. It is miscible with water and alcohol, forms a characteristic compound with lead ( $PbC_3H_7PO_6$ ), and can be made from glycerol by the action of phosphoric acid. The acid and its salts are used in medicine, in the mistaken belief that, being a biological product, it is more readily absorbed than other compounds of phosphorus. (See Brain Matter.)

**GLYCERYL** — The trivalent radical  $\dot{C}H_2\dot{C}H\dot{C}H_2$  which is combined in fats with three similar or dissimilar acidic radicals such as stearyl, palmityl, oleyl, etc. (See Glycerol, Oils, and Fats.)

**GLYCINE (Glycocoll, Aminoacetic Acid)** ( $CH_2NH_2COOH$ ) — A white, crystalline substance of sweet taste and m.p. about 233° C. with decomposition; soluble in water, and behaves both like a base and an acid, forming salts. It can be prepared chemically by several methods, as, for example, by the hydrolysis of glycocholic acid,  $C_{26}H_{43}O_6N + H_2O = C_{24}H_{40}O_5$  (cholic acid) +  $CH_2NH_2COOH$  (glycine), but it is especially interesting when considered as a derivative of wool and silk and as a product of the hydrolysis of albuminous bodies, because it is believed that a mixture of aminoacids, together with sufficient amounts of fat, starch, sugar, and the necessary saline bodies, will maintain life without the use of proteins. (See Shankman *et al.*, *J. Biol. Chem.*, **168**, 51 (1947); Albumins, Amino-acids, Bile, Foods, Polypeptides, and Vitamins.)

**GLYCOCHOLIC ACID** ( $C_{26}H_{43}O_6N$ ) — See Bile, and Glycine.

**GLYCOCOLL** — See Amino-acids, and Glycine.

**GLYCOGEN** ( $C_6H_{10}O_5$ )<sub>n</sub> — An amylaceous or dextrin-like substance, presenting much similarity to starch, contained in yeast cells and the liver and placenta of animals. It combines with water to form a gummy body, and its aqueous solution rotates polarized light to the right four times as much as dextrose. It changes rapidly into glucose, and when boiled with dilute acids it is changed into maltose. As ordinarily prepared, it is impure and has a considerable phosphorus content. As a heart content it is stated to be lost during work and disappears when that organ is exhausted. Activity is retained the longer the richer the heart is in glycogen. (See *An Introduction to the Chemistry of Carbohydrates*, by Honeyman (Clarendon Press, Oxford).)

**GLYCOL DINITRATE** — See Nitroglycol.

**GLYCOLIC ACID (Hydroxyacetic Acid)** ( $CH_2OH.COOH$ ) occurs naturally in the juice of the sugar-cane, in unripe grapes and the leaves of the wild vine, and may be prepared in a number of ways, including the oxidation of glycol. It is a colourless, crystalline, deliquescent substance, which melts at 79° C., and is soluble in water and alcohol. It has attracted attention as a possible substitute for tartaric acid in dyeing and calico-printing, processes for its production being based upon the decomposition of trichlorethylene by alkali under autoclave conditions and upon the electrolytic reduction of oxalic acid. By the action of nitric acid it is converted into oxalic acid.

**GLYCOLS** — Substances containing the grouping  $=C(OH)-C(OH)=$ ; that is, compounds possessing a hydroxyl group on each of two adjacent carbon atoms. (See Ethylene Glycol.) 1,2-Propandiol or propylene glycol ( $CH_3.CHOH.CH_2OH$ ) is a liquid, of b.p. 188° C., sp. gr. 1.040, and infinitely miscible with water or in ethanol.

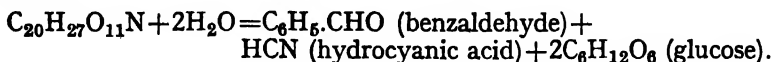
**GLYCOL ETHERS**, such as  $C_2H_4(OCH_3)_2$ , are for the most part colourless liquids of ethereal odour, being good solvents of cellulose nitrate, and of cellulose acetate. The monophenyl ether of ethylene glycol, known as "Phenoxytol" has a reputation as a bacteriostatic agent. Many others are used in the plastics industry as solvents. (See Monobutyl, Monoethyl, and Monomethyl Ethers of Diethylene and of Ethylene Glycols.)

**GLYCOSIDES** — A class of organic compounds found present in many vegetable tissues, which are resolved by hydrolysis (as effected by the action of enzymes, acids, or alkalis) into a sugar (usually glucose) and other organic substances. Some give arabinose and others rhamnose, and they are classified according to the sugar produced from them by hydrolysis, those giving rhamnose, for instance, being termed rhamnosides, and so forth.

**Æsculin** ( $C_{15}H_{16}O_9$ ) — Contained in the horse-chestnut bark.

**Amygdalin** ( $C_{20}H_{27}O_{11}N$ ) is a white, crystalline glucoside found present in the bitter almond, also in apricot and peach kernels; it has 16\*

been synthesized, and it is decomposed in the presence of water by the action of an enzyme (emulsin) contained in the tissue of the almond as follows :



**Arbutin** ( $\text{C}_{12}\text{H}_{16}\text{O}_7$ ), from the leaves of the pear-tree, the pear-berry, and the dried leaves of *Saxifraga crassifolia*, resolved by emulsion into tetramethyl glucose and hydroquinone. (See Hydroquinone.)

**Capsularin** ( $\text{C}_{22}\text{H}_{36}\text{O}_8\cdot\text{H}_2\text{O}$ ), previously named corchorin, from the seeds of *Corchorus capsularis* or jut leaf, which yields a substance of composition  $\text{C}_{16}\text{H}_{26}\text{O}_3$  upon hydrolysis.

**Castelin** ( $\text{C}_{16}\text{H}_{22}\text{O}_8\cdot 3\text{H}_2\text{O}$ ), from *Castela nicholsoni* of the natural order Simarubaceæ, which yields castelagenin ( $\text{C}_9\text{H}_{12}\text{O}_3$ ) upon hydrolysis, accompanied with a bitter principle named castelamarin ( $\text{C}_9\text{H}_{14}\text{O}_3$ ).

**Coniferin** ( $\text{C}_{16}\text{H}_{22}\text{O}_8\cdot 2\text{H}_2\text{O}$ ), in the cambium sap of various fir-trees (*Coniferæ*), and a source of vanillin. (See Vanilla.)

**Cornin** ( $\text{C}_{19}\text{H}_{21}\text{O}_9\cdot\text{OCH}_3$ ), from the root bark of *Cornis florida* L. or dog-wood.

**Datiscin** ( $\text{C}_{21}\text{H}_{24}\text{O}_{11}$ ) occurs to about 6 to 10 per cent. in the dry weight of the roots and leaves of *Datisca cannabina* L.

**Delphinin** — See Delphinin, and Plant Colouring Matters.

**Digitonin**, **Digitalin**, and **Digitoxin** — See Digitalis.

**Frangulin** (**Buckthorn**) ( $\text{C}_{21}\text{H}_{20}\text{O}_9$ ) from *Rhamnus frangula* bark. (See Persian Berries.)

**Fraxin** ( $\text{C}_{16}\text{H}_{18}\text{O}_{10}$ ), from *Fraxinus excelsior*.

**Gentiopicrocin** ( $\text{C}_{16}\text{H}_{20}\text{O}_9$ ), from the root of the species *Gentiana*. (See Gentian.)

**Glycyrrhizin** — See Liquorice.

**Hederin** ( $\text{C}_{42}\text{H}_{66}\text{O}_{11}$ ), from ivy. (See Hederin.)

**Hesperidin** ( $\text{C}_{50}\text{H}_{60}\text{O}_{27}$ ) is a constituent of unripe oranges, which yields glucose, etc., upon hydrolysis.

**Indican** ( $\text{C}_{14}\text{H}_{17}\text{O}_6\text{N}$ ), from which indigo is made. (See Indigo.)

**Melilotoside** — From *Melilotus altissima*, etc. ( $\text{C}_{15}\text{H}_{18}\text{O}_8\cdot\text{H}_2\text{O}$ ), which yields coumaric acid and dextrose.

**Ouabain** — See same.

**Phloridzin** ( $\text{C}_{21}\text{H}_{24}\text{O}_{10}$ ) is a constituent of the root bark of apple, pear, cherry, and plum trees. (See Phloridzin.)

**Picrocrocin** ( $\text{C}_{38}\text{H}_{66}\text{O}_{17}$ ) is contained in saffron. (See Saffron.)

**Populin** ( $\text{C}_{20}\text{H}_{22}\text{O}_8$ ) is contained in the aspen. (See Populin.)

**Purapurin** — An alkaloid-glucoside found in *Solanum aviculare*.

**Quercitrin** ( $\text{C}_{21}\text{H}_{22}\text{O}_{12}$ ) — See Quercitrin, and Rutin.

**Rhamnicoside** ( $\text{C}_{26}\text{H}_{30}\text{O}_{15}\cdot 4\text{H}_2\text{O}$ ) — Found in the bark of the stem of the purgative buckthorn—the source of China green.

**Rubian** — Contained in madder. (See Madder, and Rubian.)

**Rutin** ( $\text{C}_{27}\text{H}_{30}\text{O}_{16}$ ) — Contained in rue. (See Rutin.)

**Salicin** ( $\text{C}_{13}\text{H}_{18}\text{O}_7$ ) — Present in the bark of the willow and in poplar buds. (See Gaultheria Oil, Salicin, and Salicylic Acid.)

**Saponin** — See Saponins.

**Scammonin** ( $C_{34}H_{56}O_{16}$ ) — See Gums and Resins.

**Sinigrin** ( $C_{10}H_{16}O_9NS_2K$ ) — Contained in black mustard seeds. (See Mustard.)

**Solanin** ( $C_{54}H_{96}O_{18}N_2$ ) — From *Solanum sodomacum*. (See Solanin.)

**Strophanthin** ( $C_{31}H_{48}O_{12}$ ) — See Strophanthus.

**Syringin** ( $C_{17}H_{24}O_6$ ) — The glucoside of syringa.

**Tannin** — See Tannins.

**GLYCURONIC ACID** ( $CHO(CHOH)_4COOH$ ) — Obtained from saccharic acid by reduction with sodium amalgam. It is theoretically derived from dextrose by the oxidation of the primary alcohol group, whereas gluconic acid is obtained by the oxidation of the aldehyde group.

**GLYCYRRHIZIN** — See Liquorice.

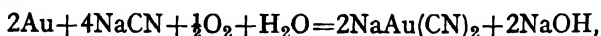
**“ GLYPTAL ”** — A synthetic resin of flexible and durable character made by heating a mixture of phthalic anhydride and glycerine. In various modified forms it is used as a base for finishing and protecting paints, varnishes, lacquers, and other surfaces, also for electrical insulating purposes, and as a shellac substitute or binder for all rigid mica insulation. Some products of this kind are marketed under the name of “ Paralac.”

**GNEISS** — A laminated mineral of granite character containing mica.

**GOA POWDER** — See Chrysarobin.

**GOLD** (Au) and its Compounds — Atomic weight, 197.2. See Elements for other data. Gold is widely distributed in nature, and is found for the most part in the free metallic condition in quartz veins and alluvial deposits resulting from the gradual disintegration of gold-bearing (older sedimentary or plutonic) rocks. It is extracted from quartz by crushing and amalgamation with mercury, and from alluvial deposits by mechanical washing with water, the water carrying away the lighter associated substances and leaving the heavier gold behind. When the amalgam process is used, the gold is obtained from the amalgam by distilling off the mercury, the gold being left behind.

There are other methods of extracting gold from its ores, including one used on a very large scale, in which potassium or sodium cyanide is the active agent employed. The crushed ore in a finely divided condition, or that from which the bulk of the gold has been already extracted by the amalgamation process, is treated with a solution of the cyanide containing from  $\frac{1}{4}$  to 1 per cent. while freely exposed to the air. This dissolves the gold according to the equation (using sodium cyanide) :



and is afterwards precipitated from the solution by passage through vessels containing metallic zinc dust or shavings or by electrolytic action (using lead-foil cathodes for that purpose) and subsequently fused.

When zinc is used for this purpose, the solution containing the gold in the form of a double cyanide undergoes chemical change as follows

(when NaCN is used) :  $2\text{NaAu}(\text{CN})_2 + \text{Zn} = 2\text{Au} + \text{Na}_2\text{Zn}(\text{CN})_4$ , excess of sodium cyanide being essential in this case. The gold is deposited on the zinc shavings, and can be purified from the zinc and other impurities by treatment with sulphuric acid or nitre cake, after which it is pressed, calcined, and melted down.

Gold is comparatively soft, yellow in colour, and the most malleable and ductile of all metals, admitting of being beaten into an extremely fine leaf form, which is used for gilding and other purposes. It can be beaten out into sheets so thin that 280,000 are required to make one inch in thickness. It is reported that 25 sheets of British leaf contain 5 grains of gold, while a similar number of Nuremberg (German) sheets contain only 3 grains. It can be prepared in colloidal form by several methods, by arcing gold electrodes under water or by reduction of gold salts. (See Purple of Cassius.)

Gold is not attacked by acids, with the exception of aqua regia (nitrohydrochloric acid), in which it dissolves, forming auric chloride ( $\text{AuCl}_3$ ).

#### GOLD, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

					Millions of Fine Ounces (1 Ounce equals 480 Grains or 31.1 Grams)
Country					
U.S.S.R.	..	..	..	..	5.3
Canada	..	..	..	..	4.6
U.S.A.	..	..	..	..	4.3
Mexico	..	..	..	..	0.8
					9.7
Colombia	..	..	..	..	0.5
Philippines	..	..	..	..	0.9
Korea ..	..	..	..	..	0.8
Japan ..	..	..	..	..	0.7
					2.4
Union of South Africa	..	..	..	..	12.2
Southern Rhodesia	..	..	..	..	0.8
Gold Coast	..	..	..	..	0.7
Belgian Congo	..	..	..	..	0.5
					14.2
Australia	..	..	..	..	1.5
Sum of above	..	..	..	..	33.6
WORLD PRODUCTION	..	..	..	..	37.7

Alloyed with copper and silver, it is largely used for coinage and other applications, including dentistry and the preparation of amalgams. Pure gold is described as 24-carat gold, whilst 18-carat gold consists of 18 parts of gold and 6 parts copper or silver. In this country the legal standard is 22-carat gold, and English gold coin consists of 11 parts gold and 1 part copper.

"Gold amalgam" (Au,Ag,Hg) is a mixture of gold, silver, and mercury containing about 40 per cent. gold.

Electro-gilding of other metals is carried out by using a solution of the double cyanide of gold and potassium ( $\text{KAu}(\text{CN})_2$ ).

**Gold oxide**, or auric oxide ( $\text{Au}_2\text{O}_3$ ), is a brown powder, insoluble in water, and combines with ammonia to form a substance of indefinite composition named *fulminating gold*, which explodes easily when heated to  $100^\circ \text{C}$ . or struck with a hammer. Other oxides are gold dioxide ( $\text{Au}_2\text{O}_2$ ) and aurous oxide ( $\text{Au}_2\text{O}$ ).

There are two **chlorides**, auric chloride ( $\text{AuCl}_3$ ) and aurous chloride ( $\text{AuCl}$ ), both of which are soluble in water, the former being the more important. It is formed when gold is dissolved in aqua regia, or by the action of chlorine on gold leaf, and can be obtained in yellowish-red crystals having the composition  $\text{AuCl}_3 \cdot 2\text{H}_2\text{O}$ , which lose their water of crystallization upon heating and change to a brown mass. This trichloride is used in photography and gold-plating. The double chloride, potassium gold chloride ( $\text{AuCl}_3 \cdot \text{KCl} \cdot 2\text{H}_2\text{O}$ ), is a soluble, yellow, crystalline salt used in photography and for painting porcelain and glass.

**GOLDBEATER'S SKIN** — Peritoneal membrane from the intestinal tube of the ox and other animals, soaked in a weak solution of potash; after washing it is stretched and beaten out with a hammer, and finally treated so that it cannot undergo putrefaction.

**GOLDEN SULPHIDE** — See Antimony, and Schlippe's Salt.

**GOMMIER RESIN** — See Gums and Resins.

**GONADOTROPHIN, CHORIONIC** ("Pregnyl," "Gonan") — A hormone, extracted from the urine of pregnant women, which has the property of stimulating the gonads. In the preparation of chorionic gonadotrophin, the pregnancy urine is first adjusted to  $\text{pH}$  6 and inert material is precipitated by the addition of 50 per cent. of ethyl alcohol and removed by filtration; the reaction of the filtrate is then adjusted to  $\text{pH}$  5 and ethyl alcohol is added until the concentration is between 80 and 90 per cent.; after allowing the liquid to stand for several hours the precipitate is collected, washed successively with alcohol and ether and subsequently dried *in vacuo*.

Chorionic gonadotrophin is standardized biologically by comparing its activity with that of a Standard Preparation of Chorionic Gonadotrophin, the international unit being the gonadotrophic activity contained in 0.1 mg. of the Standard Preparation. The assay is carried out by determining the increase in weight of the ovaries of immature female rats following the administration of chorionic gonadotrophin daily for five days and comparing the results with those

obtained by administration of the Standard Preparation to a similar group of immature female rats.

Chorionic gonadotrophin is used in medicine for the treatment of a variety of conditions arising from hypo-activity of the gonads, such as cryptorchidism or undescended testes, habitual abortion, etc.

The presence of gonadotrophic substances in pregnancy urine is the basis of various tests for pregnancy. In the Ascheim-Zondek test, immature female mice receive injections of the urine and the ovaries are examined after five days. The presence of hæmorrhagic follicles or of corpora lutea indicates that the urine contains gonadotrophic substances and, therefore, that the subject is pregnant. It has been found more convenient to use *Xenopus* toads for the test since in the case of these animals, ovulation can be induced within 24 hours. For a description of the isolation of chorionic gonadotrophin from human pregnancy urine and its biological action, see L. Claesson, B. Hogberg, T. Rosenberg, and A. Westman, *Acid. endocrinol.*, 1, 1 (1948).

**GONADOTROPHIN, SERUM** ("Gestyl," "Serogan") — A follicle-stimulating hormone, obtained from the serum of pregnant mares. In the preparation of serum gonadotrophin, blood is collected from mares between the sixtieth and seventy-fifth days of pregnancy and the plasma is separated by allowing the oxalated blood to stand overnight. The reaction is then adjusted to pH 9 by the addition of sodium hydroxide and inert protein is precipitated by the addition of alcohol. After filtration, the alcoholic strength is increased to 70 per cent., the reaction is adjusted to pH 5 and the liquid is allowed to stand for several hours. The precipitate is collected and further purified by dissolving it in water, adjusted to pH 9, and adding alcohol to precipitate inert protein. The reaction is again adjusted to pH 5 and the gonadotrophin precipitated by the addition of more alcohol, collected and dried *in vacuo*.

Serum gonadotrophin is assayed biologically by comparing its activity with that of a Standard Preparation of Serum Gonadotrophin, the international unit being the gonadotrophic activity contained in 0.25 mg. of the Standard Preparation. The test is carried out on immature female rats as described under Chorionic Gonadotrophin. It is used in medicine for the treatment of conditions arising from deficiency in activity of the pituitary gland and gonads.

For a description of the isolation of chorionic gonadotrophin from human pregnancy urine and its biological action, see L. Claesson, B. Hogberg, T. Rosenberg, and A. Westman in *Acid. Endocrinol.*, 1, 1 (1948).

**GONAKIE** (*Acacia Adamsonii*) — Found in Southern Mauritania and Northern Senegal, the pods of which produce a tanning material useful as a substitute for sumac.

"**GONAN**" — See Gonadotrophin.

**GONIOMETER** — An instrument for measuring the angles between the faces of crystals.

**GOOCH CRUCIBLE** — See Crucibles.

**GOOSE FAT** is stated to have m.p. 29° to 31° C. ; sap. v. 192·6 ; and i.v. 72·77. It separates on long standing, the solid part of which has an iodine value of 52·3, and makes up 15 per cent. of the whole, while the liquid part has an iodine value of 77, and consists mainly of triolein. Another report gives the stearic acid content as 3·8 per cent., palmitic acid 21·2 per cent., and oleic acid 72·3 per cent.

**GOSSYPIMUM** — See Cotton.

**GRAHAM'S LAW** — See Gas Laws.

**GRAINS (Brewers')** — See Beer, Malt, and Wheat.

**GRAINS OF PARADISE (Melleguetta, Guinea Pepper)** — The seeds of *Aframomum Melegueta* (N.O. Zingiberaceæ), a plant grown in Ceylon and on the western coast of Africa. Used as a condiment and in veterinary medicine.

**GRAM-ATOM** — The atomic weight of an element expressed in grams.

**GRAM-EQUIVALENT** — The atomic weight of an element expressed in grams and divided by its valency, for example, zinc has atomic weight of 65·4, and valency of 2, so that 65·4 grams of zinc divided by 2 equals 32·7 grams, or the equivalent weight of zinc. It is the weight that corresponds chemically to or is "equivalent" to 1·0 gram of hydrogen in acid or base reactions.

**GRAM (Gramme, G., Gm., Grm. (but not Gr.))** --- See Weights and Measures.

**GRAMICIDIN** — A polypeptide antibiotic, being one of the two constituents of tyrothricin produced by strains of *B. brevis*, a spore-bearing organism occurring in soil. It possesses antibacterial activity against Gram-positive organisms but is too toxic for systemic administration (see Lewis, Dimick, and Feustel, *Ind. Eng. Chem.*, **37**, 996 (1945)). Treatment of gramicidin with formaldehyde has been found to reduce its toxicity (see Lewis *et al.*, *Science*, **102**, 274 (1945)). A cyclopolypeptide, differing from gramicidin but isolated from soil bacteria has been described by Russian workers, who named their compound Gramicidin S (see Sanger, *Biochem. J.*, **40**, 261 (1946) ; and Gause, *Lancet*, **2**, 46 (1946)). (See "The Chemistry of Antibiotic Substances other than Penicillin," by Oxford (*Ann. Reviews Biochemistry*, **14**, 733 (1945)) ; Bacteria, Penicillin, and Tyrocidin.)

**GRANITE** — Rocks of felspar and mica in a mass of quartz, often associated with other minerals ; m.p. variously given as 1,100° and 1,240° C.

**GRAPE-SEED OIL** is a yellow, fixed, edible oil of pleasant odour and taste expressed or extracted from the seeds of *Vitis vinifera* ; yield 9 to 12 per cent. from fresh pips or 15 to 17 per cent. in the dry state. It has a solidifying-point of -10° to -13° C. ; m.p., 24° C. ; sp. gr., 0·92 to 0·935 ; sap. v., 178 to 180 ; ref. ind., 1·4713 at 25° C., and i.v., 94 to 96·5. It is soluble in benzol and carbon disulphide, and used as an illuminant, lubricant, food, for soap-making, also as a substitute for

castor oil in respect of some applications, although liable to speedy rancidity.

As obtained from the United States Concord grapes, the oil has been given the following values: sp. gr. at 25° C., 0.9204; solidifying at -22° to -24° C.; sap. v., 192.2; and i.v., 135.8; containing 53.6 per cent. linolin, 35.9 per cent. olein, 5.2 per cent. palmitin, 2.2 per cent. stearin, and unsaponifiable matter 1.6 per cent. It is stated to be, when refined, as good as soya-bean oil, and can be used for making oleo-margarine, also for admixture with linseed oil in paint-making.

**GRAPE SUGAR (Glucose)** — See Glucose, Sugars, and Carbohydrates.

**GRAPHITE** — See Carbon, and Kish.

**GRASS** — See Ensilage, and Paper.

**GRASS OILS** — Volatile essential oils, including citronella oil, lemon grass oil, geranium oil, ginger grass oil, etc., derived from a number of different plants. (See Essential Oils.)

**GRAVITIES** — See Densities, Specific Gravity, and Hydrometer.

**GRAVITY DIE-CASTING** — Production of cast articles by feeding molten metal under the action of gravity into permanent metal moulds. (See *Gravity Die-Casting Technique*, by G. W. Lowe (Hutchinson's Scientific and Technical Publications, London).)

**GREASES** — Axle greases are of two classes, namely, (1) those consisting essentially of calcium resinate dissolved in rosin oil, and (2) those consisting of lubricating mixtures being solid or semi-solid emulsions of fats, fatty oils, mineral oils, and rosin oils, with lime-soda or metallic soaps. Boner (*Ind. Eng. Chem.*, **29**, 58 (1937)) gives the properties of soaps from 18 metals and 2 fatty acids in connection with a discussion of the characteristics of metallic soaps used in thickening mineral oils for lubricants. (See Lubricants.)

**GREEN OIL** — A heavy crude fraction of creosote oil containing anthracene, chrysene, carbazole, etc., distilled from coal tar, from which the anthracene and associated bodies can be separated by cooling. (See Coal.)

**GREEN VITRIOL (Green Copperas)** — Common name for ferrous sulphate crystals. (See Iron (Ferrous Sulphate).)

**GREENOCKITE** — See Cadmium.

**GREY ANTIMONY ORE (Stibnite)** — See Antimony

**GRIGNARD REAGENTS** — Organometallic compounds of magnesium, such as magnesium methyl iodide, used in organic syntheses. The medium used is anhydrous ether, which is a hazard as to fire and explosion. The reagent is prepared by adding carefully dried magnesium chips to anhydrous ether, then adding a halogenated hydrocarbon. The simplest reagent, namely, methyl magnesium iodide, has the composition  $\text{CH}_3\text{MgI} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ . The following are important applications: Addition of water causes the formation of the hydrocarbon corresponding to the halogenated hydrocarbon used; addition

of an aldehyde causes the formation of secondary alcohol; and addition of a ketone causes the formation of tertiary alcohol. See article on "Grignard Reaction" in *Van Nostrand's Scientific Encyclopedia* (D. Van Nostrand Co., New York; Chapman and Hall, London).

**GRINDING** — See Crushing and Grinding.

**GRINDSTONE** — A highly cemented, tough, natural sandstone.

**GROUND-NUT OIL** — See Arachis Oil.

**GUAIACOL** — A phenolic substance consisting chiefly of the mono-methylether of catechol,  $C_6H_4(OH)(1)(OCH_3)(2)$ , and occurring as a colourless, refractive, inflammable oily liquid or as colourless crystals having a penetrating odour. It is obtained by distillation from wood creosote, by dry distillation of guaiacum resin, or by synthesis. A process designed by Azaretti obtains it from anisidine sulphate by diazotization and decomposition of the diazo-sulphate in the presence of copper sulphate, with a yield of 72 to 73 per cent. It is soluble in water, alcohol and ether; sp. gr. 1.16 to 1.25; m.p.  $28^\circ C.$ ; and b.p.  $205^\circ C.$  It has been used in medicine as an antiseptic and deodorant, but its chief use is as an intermediate in the manufacture of coumarin and vanillin.

**GUAIACUM RESIN** — A dark green or black resin extracted from Guaiacum Wood; soluble in alcohol, acetone, and ether, and having mildly laxative and diuretic properties. An optically active substance named guaiaretic acid ( $C_{20}H_{24}O_4$ ) has been isolated from the resin. (See Guaiacol, and Guaiacum Wood.)

**GUAIACUM WOOD** — The heart-wood of *Guaiacum officinale* or of *Guaiacum sanctum* (N.O. Zygophyllacæ), trees which grow in Jamaica and other West Indian Islands. It has a sp. gr. of 1.336 and is used for making taps and vessels which are more resistant to many chemical liquids than ordinary wood. It contains from 18 to 25 per cent. of resin. (See Guaiacum Resin.)

**GUAIAC-WOOD OIL** — A thick, viscid oil, apt to become crystalline, distilled from the wood of some species of guaiacum, known as "balsam wood," and "holy wood" in South America. It is soluble in alcohol and ether, has a sp. gr. of about 0.96 to 0.98 at  $15^\circ C.$ , opt. rot.  $-6^\circ$  to  $-7^\circ$  at  $20^\circ C.$ , and is used in perfumery.

**GUAIACYL CARBONATE (Duotal)** ( $C_{15}H_{14}O_5$ ) — A white, crystalline powder prepared by passing carbonyl chloride into a solution of guaiacol in sodium hydroxide solution, and recrystallization of the carbonic ester thus obtained; insoluble in water, soluble in alcohol and ether; m.p.  $85^\circ$  to  $88^\circ C.$  It has been used in medicine as an antiseptic and antipyretic.

**GUANIDINE (Iminocarbamide)** ( $NH:C(NH_2)_2$ ) — A crystalline substance, soluble in water, obtainable by various processes, and which yields urea and ammonia upon hydrolysis,  $CN_3H_5 + H_2O = CON_2H_4 + NH_3$ . It occurs among the hydrolytic products of certain amino-acids. Its sulphanilamide derivative, sulphaguanidine, is used in the treatment of infections of the gut. (See Sulphanilamide, and Urea.)

**GUANO** — Excrement of sea-fowl from islands near the coast of Peru and Chile and elsewhere, consisting largely of calcium phosphate, and used as a fertilizer. (See Coprolites, and Fertilizers.)

**GUAVA** — The fruit of *Psidium guajava* (Linn., N.O. Myrtaceæ). Various species occur in S. America, E. and W. Indies, China, etc., in which the proportions of flesh, seed, and pectic juice vary very much. Specimens give from 58 to 85 per cent. flesh, and the flesh contains proportions of glucose, lævulose, and sucrose. An oil is contained in the seeds (about 8.4 per cent.), which has a sp. gr. of 0.927, i.v. 131.1, and sap. v. 197.1.

**GUAYULE** — A rubber-secreting shrub (*Parthenium argentatum*) of some importance in the semi-desert south-western States of U.S.A. and Northern Mexico. When the plant is 5 years old the best strains contain about 20 weight per cent. of rubber in the dried plant, and the yield of rubber per acre is reported to be 1,600 pounds and of good quality when accompanying resins are removed.

**GUIGNET'S GREEN** — A hydrated chromium sesquioxide of indefinite composition, made by fusion of potassium dichromate with boric acid followed by decomposition with water ; used as a mineral pigment.

**GUMS and RESINS** — These include a variety of substances, of ill-defined chemical composition, obtained from vegetable sources. Gums are insoluble in organic solvents such as alcohol and ether, but are soluble or swell in water to form viscous, adhesive solutions or gelatinous masses. On hydrolysis with dilute mineral acids, they yield pentose sugars such as arabinose and xylose, and a hexose sugar, galactose. In the original gum, these sugars are combined by glycosidic linkages with an organic acid which may be free or in the form of its potassium, calcium, or magnesium salt. Gums also contain up to 5 per cent. of inorganic matter and small amounts of free sugars and nitrogenous substances. Gums are formed by shrubs and trees, especially those belonging to the Leguminosæ, Rosaceæ, Rutaceæ, and Sterculiaceæ, and are produced by the conversion of cell tissues, probably by enzymatic action. Some, such as acacia, are formed only after injury to the plant tissues and can be regarded as pathological products. Mucilages are normal plant products, secreted by specialized cells.

Resins are hard, amorphous solids or, occasionally, semi-solids. They contain a high proportion of carbon but little oxygen and, on heating, first soften and ultimately burn with a smoky flame. They are insoluble in water but are usually soluble in organic solvents, such as alcohol, chloroform, or ether. Chemically, resins consist of complex mixtures of organic acids (resin acids) and alcohols (resin alcohols) which are usually aromatic in nature. Other substances present are resenes, which are neutral and are neither esters nor acids. Some resins, on hydrolysis, yield sugars, indicating that they are glycosidic in nature. Resins may be formed as a natural process in the life of the plant or as the result of injury to the tissues. Volatile oils con-

taining terpenes yield resins on oxidation and this may be the mechanism by which they are formed in nature.

Resins are mostly yellow or brown in colour ; some become electrically charged when rubbed. Hardness is an important quality, and this decreases in the following order : Congo copal, kauri, pontianic, accroides, East India, batu, Manila copal, Singapore dammar, Batavia dammar, sandarac, mastic, elemi. Descriptions of them individually will be found under their several names either below or in the main text, or under the heading of Balsams. The resins are largely used in making lacquers, varnishes, rubber substitutes, linoleum, paper and textile sizing, and adhesives.

Gum-resins, as the name implies, consist of mixtures of gum and resin formed together in the plant. They may be associated with small amounts of volatile oils, bitter principles, or enzymes. The gum present usually closely resembles acacia gum, whilst the resins consist of characteristic resin acids and alcohols.

Oleo-resins are mixtures of resin with volatile oils or similar oily liquids. Like gums and resins, they may be a normal plant product or result from injury to the tissues. Oleo-resins, in which the constituent acids are cinnamic and benzoic, are known as balsams (*q.v.*).

**Acacia (Arabic)** — The dried exudation obtained from *Acacia senegal* and other species of *Acaciæ* which grow in Arabia, Egypt, the Soudan, and Senegambia. Many varieties are known commercially but the Kordofan gum is most esteemed. Inferior varieties, known as Gum Arabic, are used in various industries. It dissolves slowly in water, and consists mainly of a mixture of calcium, potassium, and magnesium arabinates, which on hydrolysis yield arabinose, galactose, and glycuronic acid. It is used not only as an adhesive, but also as a demulcent in the preparation of a number of pharmaceutical and chemical emulsions ; also for thickening ink, in the manufacture of blacking, and in calico-printing.

**Accroides (Black-Boy Gum)** — A resin from *Xanthorrhæa* trees, indigenous in Australia ; soluble in alcohol, and used in varnish-making.

**Aloes** — See same.

**Amber** — See same.

**Ammoniacum** is a natural resin obtained from the *Dorema ammoniacum* of N.O. Umbelliferae, a native of Central Persia.

**Animi** — See Copal, below.

**Asafoetida** — A gum-resin extracted from the root of *Ferula foetida*, an umbelliferous plant which grows in Eastern Persia and Western Afghanistan. It has a strong, offensive, onion-like odour and is partially soluble in alcohol. It contains about 25 per cent. of gum and from 6 to 17 per cent. of volatile oil. The latter contains two terpenes, one of which is pinene, and two disulphides,  $C_7H_{14}S_2$  and  $C_{11}H_{20}S_2$ . The resin consists of an alcohol, asaresinotannol, partly free and combined with ferulic acid. It was formerly used in medicine as a carminative and sedative.

**Australian, or Wattle Gum**, exuded from several species of acacia, yellow to reddish-brown in colour.

**Barbary** — Product of the African (Morocco) *Acacia gummifera*.

**Bassora** — From the *Acacia leucophlœa*. Somewhat similar to tragacanth. Varieties are Indian, karaya, and kuteera gums.

**Batu** — A variety of East India resin (see below).

**Benzoin** — A resin obtained by incision from the stem of *Styrax Benzoin* and of *S. paralleloneurus* (Sumatra Benzoin) or of *S. tonkinensis* (Siam Benzoin). It is a brittle solid consisting of white or pale pink tears embedded in a reddish-brown mass and having a pleasant balsamic odour; partially soluble in alcohol and in ether, the insoluble matter being inorganic impurities. It consists of various esters of benzoic and cinnamic acids, together with the free acids. It is used in pharmacy and in the manufacture of varnishes.

**British Gum** — See Dextrin, and Starch.

**Canada** — See Balsams.

**Cannabis** — See same.

**Cape** — From the *Acacia horrida* (Willd.).

**Colophony (Resin, Rosin, Amber Resin)** — The resin remaining after distillation of turpentine from the crude oleo-resin obtained from *Pinus palustris* and various other species of *Pinus* which grow in Europe and the U.S.A. It is soluble in alcohol, ether, benzene, and carbon disulphide and consists chiefly of three isomeric abietic acids. Colophony is graded according to colour, from B, the darkest, to WW, the lightest, and is used in various industries such as process engraving, sizing paper, oilcloth and linoleum manufacture. It has the property of combining with alkali to form a soap and is particularly used in the soap industry. The acid value of resin depends upon the variety, ranging from 131 to 180; sap. v. 146 to 195; i.v. 55 to 184. The saponification value of the American resin ranges from 170 to 180 and the iodine value is about 122. All these values are alleged to undergo change if the resin is kept in powdered form in closed containers.

When subjected to destructive distillation, it is split up into a number of products, including "rosin spirit" and "rosin oil" which are distilled over, whilst a pitch remains in the retort. When heated with Japanese acid clay, it is said to yield a distillate containing some petroleum hydrocarbons.

**Congo** — See Copal below.

**Convolvulin** — See Convolvulin, and Scammony (below).

**Copaiba** — See Balsams, and Copaiba Oil.

**Copal (Zanzibar Copal, Gum Animi)** — A fossil resin obtained from *Trachylobium Hornemannianum*. It varies in colour from pale yellow to reddish-brown; soluble in alcohol, partially soluble in benzene and chloroform. American Copal is exported from Brazil and is derived from *Hymenæa Courbaril*; it is pale brown in colour and of pleasant odour. West African Copal is obtained from *Copaifera Guibourtiana*. Varieties of Copal can be identified to some extent by microscopic examination and they differ in their melting-points (150° to 315° C.). On exposure to air, copal absorbs oxygen and becomes more soluble in organic solvents; the solubility is also increased by melting the

resin at the lowest possible temperature. Copal is used in making high-quality varnishes and cements. (See Gum Manilla, and Varnishes.)

**Cowrie** — See Gum Kauri, and Gum Copal.

**Dammar (Dammara Resin)** — There are several varieties of this resin, the commonest being East Indian or Singapore Dammar which is obtained from various species of *Shorea*, *Hopea*, and *Balnocarpus* grown in the Eastern Archipelago. It melts at about 120° C. and is soluble in turpentine, alcohol, and ether and is used in the manufacture of sticking-plasters, varnishes, and lacquers. Dammar has also been known as Manila Copal.

Black Dammar is a black resinous exudation obtained from *Canarium strictum* Roxb., a native of S. India; it melts at about 100° C. and is used in making bottling-wax, varnishes and as a substitute for Burgundy Pitch. On distillation, it yields a deep blue oil (80 to 85 per cent.) and a combustible gas (6 to 7 per cent.) the colour of the oil being attributed to a substance named azulene. The resin is soluble in benzene and turpentine and partially soluble in alcohol.

Malayan Dammar Penak is a product of the State of Negri Sembilan. (See Penak Resin.)

**Dragon's Blood** — See Balsams.

**East India** — Resin from *Dipterocarpus* growing in the East Indies, and widely used. Batu is one variety. It is soluble in paraffin, cyclo-paraffin, and aromatic hydrocarbons, and insoluble in ketones, alcohols, and esters.

**Elemi** is an East and West Indian oleo-resinous product from various terebinthinous trees, including *Canarium luzonicum*, a native of Manila, and the *Amyris elemifera* (Dutch Settlements); used in making varnishes and lacquers. Manila elemi is colourless and honeylike in character and of aromatic odour. It yields about 20 per cent. of elemi oil containing one of the higher terpenes. Used in lacquers and varnishes.

**Euphorbium** — Resin from *Euphorbia resinifera* of Mexico.

**Frankincense** — See Olibanum (below).

**Galbanum** — A gum-resin obtained from *Ferula galbaniflua* and possibly other species of *Ferula* grown in Persia. It has a sp. gr. of 0.905 to 0.995 and occurs in the form of hardened tear-like drops of light green colour and aromatic odour. It contains from 5 to 20 per cent. of volatile oil and about 20 per cent. of gum.

**Gamboge** — A gum-resin obtained from *Garcinia morella* procured almost entirely from Siam, originally from the province of Cambodia which gives its name thus, first *camboge* then *gamboge*. When the leaves and shoots of the tree are broken off, the gum resin issues as droplets and is collected. The moisture is evaporated, and when the residue is sufficiently concentrated it is rolled into cylinders, or cast by pouring into the hollow parts of bamboo. Gamboge is of a bright orange-yellow colour, and is used principally as a pigment.

**Ghatti** — The product of *Anogeissus latifolia* (India and Ceylon), resembling gum acacia, and of great hardness.

**Gilead (Mecca)** — See Balsams.

**Gommier** — A resin obtained from *Dacryodes hexandra* and various

sandarac is derived from *Callitris verrucosa* and is softer ; it contains a larger proportion of inactive pimaric acid and pinene.

**Scammony Resin (Ipomœa Resin)** — A mixture of resins obtained from the dried root of *Ipomœa orizabensis*, Ledanois, a climbing plant growing in the Mexican Andes. It contains the methylpentosides of jalapinic acid and its methyl ester and is used medicinally as a drastic purgative. The original scammony resin, obtained from *Convolvulus Scammonia*, and coming from the Levant, is now a scarce commodity.

**Senegal** is obtained from a species of acacia in the French colony of Senegal, and makes a stronger mucilage than gum arabic (acacia). It is the variety of acacia gum that is used in medicine, also for thickening the colours and mordants used by calico-printers.

**Shellac** — See same.

**Storax** — See Balsams.

**Tolu** — See Balsams.

**Tragacanth** — The dried mucilaginous exudation obtained from the *Astragalus gummifer* and other species of *Astragalus* which grow in Armenia, Turkey, Syria, and Persia. It is only partially soluble in water, but swells into a gelatinous mass. Its composition is not clearly known ; the water-soluble portion on hydrolysis yields arabinose, galactose, and geddic acid ; the water-insoluble portion tragacanthose, xylose and bassoric acid. It is graded into from "firsts" to "fifths" according to quality, and is used in pharmacy, in calico-printing, and for stiffening rough cloth materials. The cherry-tree furnishes a somewhat similar gum.

**Tragon** — Prepared from the carob bean ; used in the leather industry and as a thickener for certain sauces, etc. (See Locust Kernel.)

**Yacca** — A red or yellow resin from *Xanthorrhœa hastilis* of Australia. It is soluble in alcohol, but insoluble in turpentine, linseed oil, benzol, and hydrocarbon solvents generally, but dissolves readily in aqueous caustic alkaline solutions to deep red solutions, from which it can be reprecipitated by acids in a yellow flocculent form. It is used in the manufacture of dyes and photographic chemicals.

**Zanzibar** — Varieties of animi and of copal.

**Ester Gums**, such as "Abrac," are substitutes for some of the harder natural resins. They are soluble in amyl acetate, some oils, turpentine, carbon tetrachloride, etc., have acid values from 2 to 150, and are stated to be much more suitable than ordinary resin for use in making certain varnishes and enamels. To prepare them, the softer parts of the acid resins are removed by distillation in a vacuum or a current of superheated steam, and the residue is heated with an equivalent proportion of glycerol, phenol, or naphthol to a high temperature with a dehydrating agent. According to F. M. Beegle, using resin and glycerol, an autoclave is not necessary ; an aluminium vessel may be used without vacuum or pressure, and a proportion of wood oil facilitates the speed of reaction.

Resin esters can be formed with glycerol by heating together at from 280° to 300° C., and passing a current of hydrogen chloride, carbon dioxide, or air through the mixture.

Ester gums are used in making enamel paints, cellulose lacquers, and more particularly (in conjunction with tung oil) for waterproof varnishes for boats, yachts, etc., and for electrical insulation. (See "Abrac.")

**Synthetic Resins** — Of the other various types of so-called ester gums, synthetic resins, or plastics, many are obtained from phenol, cresol, acetone, casein, lignin, furfural, naphthalene, acrolein, thiourea, phthalic anhydride, etc., by the action of formaldehyde under varying conditions and are generally known as "condensation products." With respect to formaldehyde products, it has been shown that with acetone and its homologues in alkaline media, as the series rises, larger amounts of alkali and more lengthened heating are required.

Coumarone resin is made by polymerizing indene and coumarone—constituents of that fraction of coal-tar naphtha distilling between 160° and 200° C. After washing with alkali and acid to remove substances containing oxygen and nitrogen, the oil is treated with concentrated sulphuric acid in small amounts, thus bringing about polymerization and some degree of sulphonation, and upon distillation of the oily part of the product the benzol is carried over, leaving the coumarone resinous material in the retort. Alternatively other polymerizing agents, such as compounds of zinc, aluminium, and tin, can be employed.

The yellowish to red synthetic resins are not soluble in water, but are variously soluble in alcohol, naphtha, ether, turpentine, acetone, benzene, butyl alcohol, cresols, cyclohexanol, tetrahydronaphthalene, carbon disulphide, etc., and used in compounding rubber goods, lacquers, paints, inks, insulating and binding materials, domestic ware, adhesives, varnishes, for lining vessels, and as substitutes for shellac.

Synthetic resins include "Abrac," "Acrolite," Acrylic Resins, "Acryloid," "Alkilit," "Albertol," "Bakelite," "Beatl," "Coalalith," "Condensite," "Durium," "Erinoid," "Formite," "Gallilith," "Glyptal," "Indurite," "Mouldensite," "Nestorite," "Novolak," Polyvinyl Resins, "Redmanol," "Resinite," and "Synthite," most of which are described under their respective names. (See Formaldehyde Resins.)

(See "Chemistry of Synthetic Varnish Resins," by Ivey Allen *et al.* (*Ind. Eng. Chem.*, **26**, 663 (1934)) ; *The Chemistry of the Natural and Synthetic Resins*, by T. H. Barry (with others) (Ernest Benn, Ltd., London) ; *The Technology of Natural Resins*, by C. L. Mantell (John Wiley and Sons, New York) ; *Artificial Resins*, by Scheiber and Sändig (Sir Isaac Pitman and Sons, Ltd., London) ; *The Chemistry of Synthetic Resins*, by Carleton Ellis (Reinhold Publishing, Corp., New York) ; *A Chemistry of Plastics and High Polymers*, by P. D. Ritchie (Interscience Publishers, New York) ; *Phenoplasts: Their Structure, Properties and Chemical Technology*, by T. S. Carswell (Interscience Publishers, New York) ; *Synthetic Resins and Allied Plastics*, by R. S. Morrell *et al.* (Oxford University Press) ; *Synthetic Resins and Rubbers*, by Paul O. Powers (John Wiley and Sons, New York) ; *Balsams, Formaldehyde, Plastics, Vinyl Alcohol, and Varnishes.*)

**GUN-COTTON** — See Collodion Cotton, Explosives (Gun-Cotton), Nitro-cellulose, and Pyroxylin.

**GUN-METAL** — An alloy of 9 parts copper with 1 part tin.

**GUNPOWDER** — See Explosives.

**GUTTA-PERCHA** — The natural, dark, hardened juice of the Sapotacea or gutta-percha trees (*Isonarda percha* or *Isonarda gutta*) which grow in equatorial regions (Borneo, Brazil, Malaya, Singapore, Ceylon, etc.). It exudes from incisions made in the bark, and in a pure state is white, insoluble in alcohol, but soluble in carbon disulphide, carbon tetrachloride and chloroform, turpentine being a partial solvent. It is obtained from the leaves, which contain about 2·3 per cent., the twigs (0·7 per cent.), and the bark (1·2 per cent.), by heating in hot water or steaming up to about 70° C., the gutta being skimmed off the surface and subsequently washed in hot water. As thus obtained, it contains associated resins, which have to be removed by suitable solvents such as petroleum spirit. The de-resinified product is very prone to oxidation, becomes soft and impressionable when warmed in hot water at 37° C. ; exhibits a dielectric constant 2·56, melts at from 120° to 130° C. ; is largely used as an insulating material for cables and electric wires, also as a covering for golf-balls, for making belting, carboys, bottles, funnels, jugs, taps, valves, etc., in dentistry and waterproofing. When vulcanized, it does not become plastic upon warming and assumes characters resembling those of vulcanized rubber. Gutta-percha is a hydrocarbon ( $C_{10}H_{16}$ ), having near chemical relationship to turpentine, and isomeric with the hydrocarbon of caoutchouc rubber. (See A. E. Penfold on "Characteristics and Manufacture of Gutta-Percha" (*Transactions of the Institution of the Rubber Industry*, 8, 407 (1933)); and Rubber.)

**GYPSUM** — See Calcium (Sulphate).

**H ACID** — See Acid H.

**H-BOMB** — See Fusion Reaction.

**HABER PROCESS** — See Nitrogen Fixation.

**HÆMATIN** — The prosthetic group of the conjugated protein forming the red pigment of the blood, hæmoglobin, and obtained from the latter by careful hydrolysis with hydrochloric acid, the resulting hæmatin chloride having the formula  $C_{34}H_{32}O_4N_4FeCl$ . Hæmoglobin contains about 6 per cent. of hæmatin associated with about 94 per cent. of globulin. Hæmatin is closely related to chlorophyll and the same basic structure, aetioporphylin, can be isolated from each. (See *Hæmatin Compounds and Bile Pigments*, by R. Lemberg and J. W. Legge (Interscience Publishers, New York); *Recent Advances in Organic Chemistry* (Longmans, Green and Co., London); *Hæmoglobin: A Symposium* (Interscience Publishers, New York, and Butterworths Scientific Publ., London); also Chlorophyll, and Respiration.)

**HÆMATITE (Hematite)** — Iron ore of many varieties. (See Iron.)

**HÆMOGLOBIN** — See Hæmatin.

**HAFNium (Hf) and its Compounds** — Atomic weight 178·6. See Elements for other data. Hafnium was discovered, in 1923, by X-ray spectroscopy in zirconium containing minerals, which latter element it markedly resembles and with which it appears to be associated naturally to the extent of about 1 per cent., and rarely more than 2 per cent. The minerals richest in hafnium are *alvite*, *cyrtolith*, *nargecte*, and *malakon*. It appears to be the same element as the so-named celtium. Hafnium crystallizes in the hexagonal form, and is very ductile when pure.

The name hafnium was accepted (1949) by the International Union of Chemistry.

**Hafnium oxide** ( $\text{HfO}_2$ ) is more refractory than the corresponding zirconium oxide, the respective melting points being given as  $2810^\circ$  and  $2700^\circ$  C. The oxide, as derived from the nitrate by reduction with hydrogen, in association with tungsten oxide (to the extent of between 0·1 and 3 per cent.) gives to the metallic tungsten subsequently obtained by sintering the mixture in hydrogen the property of being easily drawn. (See *Rarer Metals*, by Jack De Ment and H. C. Dake (Chemical Publishing Co., Brooklyn); and Zircons.)

**HAIR** — Consists of coalesced horny cells of gelatinous character containing from 0·75 to 2 per cent. of mineral salts. (See "Hair and Fibres," by C. A. Mitchell (*Chem. and Ind.*, 49, 451 (1930)); *A Study of Hairs and Wools*, by J. Glaister (Cairo: University Press, 1931); also Fibres.)

**HAIR HYGROGRAPH** — See Hygograph.

**HAIR SALT** — See Aluminium (Sulphate).

**"HALARSOL"** — A stabilized solution of 3-amino-4-hydroxyphenyl-arsenoxide, being a remedy for syphilis and the disease known as yaws.

**HALF LIFE** — The length of time required for a radioactive element to decay to one-half its original radioactivity. This value is characteristic (a constant of nature) of each isotope, and is independent of the amount present as well as independent of the temperature and the pressure.

**HALFA (HALVA)** — See Esparto Grass.

**HALIDES** — Metallic and non-metallic combinations of the halogens, such as sodium chloride ( $\text{NaCl}$ ), silicon tetrachloride ( $\text{SiCl}_4$ ), and methyl chloride ( $\text{CH}_3\text{Cl}$ ).

**HALOGENATION** — The introduction of a halogen into a compound in substitution of hydrogen or hydroxyl, or by addition. The term is usually restricted to organic substances. (See Chlorination.)

**HALOGEN DERIVATIVES** of organic bodies are formed by the replacement, for example, of hydroxyl ( $\text{OH}$ ) or of hydrogen ( $\text{H}$ ) by a halogen; thus ethyl alcohol by the action of hydrobromic acid is converted into ethyl bromide:  $\text{C}_2\text{H}_5\text{OH} + \text{HBr} = \text{C}_2\text{H}_5\text{Br} + \text{H}_2\text{O}$ ; benzene by the action of chlorine into chlorobenzene:  $\text{C}_6\text{H}_6 + \text{Cl}_2 = \text{C}_6\text{H}_5\text{Cl} + \text{HCl}$ ; and benzoic acid by the action of phosphorus pentachloride into benzoyl chloride:  $\text{C}_6\text{H}_5\text{COOH} + \text{PCl}_5 = \text{C}_6\text{H}_5\text{COCl} + \text{POCl}_3 + \text{HCl}$ .

**HALOGENS** — See Elements.

**HALOIDS** — Salts composed of halogen elements with metals, such as sodium chloride and potassium iodide.

**HAMAMELIS** (*Hamamelis Leaves, Witch Hazel Leaves*) — The dried leaves of *Hamamelis virginiana*, a shrub growing in the United States and Canada. It contains tannin and gallic acid with a trace of a volatile oil and a bitter principle. An alcoholic liquid extract is used in medicine for its astringent properties. Distilled Witch Hazel is prepared by distilling the leaves with aqueous alcohol and contains no tannin, which remains in the residue on distillation (see Yosida, *Chem. Abst.*, **34**, 1130 (1940)). It is used as a cooling application for insect bites, stings, and bruises, but appears to have no special virtues other than those due to the alcohol it contains. A dried extract of *Hamamelis* is used as a constituent of ointments and suppositories for the treatment of hæmorrhoids.

**HANKOW WOOD OIL** — See Tung Oil.

**HANSGRIG CARBOTHERMIC PROCESS** — See Magnesium.

**HANUS REAGENT** — Ten grams iodine monobromide in 500 c.c. glacial acetic acid, used for determining iodine values, and preferred in some cases to Hübl's reagent. (See Fats.)

**HARDNESS** — See Elements for data for individual elements. A property of a substance which resists abrasion, cutting, or indentation. Compounds with unsymmetrical structure, that is, with other than cubic or hexagonal structure, are solids that are usually brittle in aggregates. See Mohs' Scale for hardness of solids and minerals; and Brinell Ball Test for that of metals; also Desch's address on "The Nature of Hardness" (*Chem. and Ind.*, **48**, 487 (1929)); and D. A. N. Sandifer on "The Pendulum Hardness Tests of Commercially Pure Metals" (*B.C.A.*, B, 1930, 1074); *Hardness and Hardness Measurements*, by S. R. Williams (American Society for Metals, Cleveland); *The Hardness of Metals and Its Measurements*, by H. O'Neill (Chapman and Hall, London); and Water Conditioning (hardness of water).

**HARTSHORN** — An old name for crude ammonium carbonate as originally obtained by distillation of horn shavings.

**HASHISH** — See Hempseed Oil, and Gums and Resins (*Cannabis*).

"**HASTELLOY**" — A series of nickel base alloys with varying percentages of molybdenum, chromium, silicon. They are exceptionally resistant to chemicals, including hydrochloric and sulphuric acids and wet chlorine. They have also outstanding high temperature properties which makes them suitable for applications in turbosuperchargers and gas turbines.

**HATCHETTINE** (*Hatchettite*) — A mineral of tallow-like and hydrocarbon character resembling ozokerite, found in some coal-beds and bogs; m.p. 115° to 170° F.

**HAUSMANNITE** ( $Mn_3O_4$ ) — A mineral of crystal system No. 2, and sp. gr. 4.72. (See Manganese Oxides.)

**HAZARDOUS CHEMICALS** are those chemicals that may cause damage to individuals or property in respect to health, fire, explosion or corrosion. The only general rule that can be stated about any or all chemicals and their potential hazards is to know the complete nature of the chemical and then to use wisdom in all things pertaining to its use.

It is advantageous to evaluate the risks accompanying the increased use of chemicals in our everyday lives. New products are continually appearing not only on the industrial market but also in over-the-counter trade to individuals. In order to reduce the hazards and to control the potential dangers strict laws have been passed and enforced concerning the labelling and marketing of all such chemicals. However, carelessness is a human frailty that cannot be legislated out of existence but it can be educated by eternal diligence. Unfortunately a chemical will always react in a given way when placed in a given set of conditions without regard to the intentions of the operator, frequently resulting in accident, loss of life, or damage to property.

The corrosive properties of chemicals are one of the big problems of industry. Fire and explosions are due to the combustible properties of certain chemicals or chemical mixtures. Inflammability is regarded as a specific property of a mixture and is independent of any particular method of ignition. Some of the limiting factors governing fires and explosions are: *flash point*, which is the lowest temperature at which a given substance will take fire when subjected to an open flame; and *ignition temperature*, which is the lowest temperature necessary for self-propagation of burning. The main difference between a fire and an explosion is the rate at which the burning takes place. For example, a jet of methane will burn in air when once ignited, but if the air and methane are first mixed in the proper proportions in a large container and then ignited the propagation of the flame through the mixture is very rapid, giving rise to a rapid gas expansion, *i.e.*, an explosion. Generally, flammable liquids and solids burn quietly in air, but some solid and liquid substances can be detonated, in which case they explode violently. These substances called explosives have an internal source of oxygen, which is one of the essential ingredients for most burning, but in special cases oxidizing substances can be substituted. For example, chlorine will support the combustion of turpentine and magnesium.

Chemicals that are most noted for their fire or explosive hazards can be classified in one of the following groups: (1) Inflammable gases. For example, hydrogen, methane, acetylene, and carbon monoxide. (2) Liquids with flash points below 80 degrees F. or 27 degrees C. such as diethyl ether, carbon disulphide, solvent naphthas, acetone, allyl chloride, methanol, ethanol, ethyl acetate, and many others. (3) Inflammable solids: (a) Solids that burn spontaneously on exposure to air, such as white phosphorus; (b) Solids that burn spontaneously on exposure to moisture, such as sodium, potassium, and sodium peroxide (this in the presence of organic matter such as paper); (c) Solids that burn when heated to moderate temperatures, such as red

phosphorus. (4) Oxidizing agents, such as potassium chlorate, potassium permanganate, sodium nitrate, and potassium nitrate, that support combustion when mixed with inflammable substances and ignited. (5) Corrosive liquids, such as nitric, perchloric, and sulphuric acids.

Fires and explosions are generally started by a spark or flame from some burning substance, from an electrical device, or by static electricity, but in some cases auto-ignition takes place due to the temperature. Protection against fire hazards consists in taking every precaution possible before working with or mixing chemicals that are potential fire or explosion hazards. These precautions consist of adequate ventilation, use of proper containers, preparing the proper atmosphere for the chemicals used, protecting electrical outlets from sparks, grounding non-conductors against static electricity, control of temperature, removal of any ignited object such as cigarettes, and removing vapours of highly inflammable substances.

If a fire starts there are two ways of stopping it: (1) To remove the supply of air from the burning mass, and (2) to lower the temperature of the burning mass until the fire is extinguished. Apparatus for best performing these two functions for the particular job should be available at all times and all personnel should be thoroughly trained in using the equipment.

The health hazard of certain chemicals, such as chlorine, mustard gas, carbon monoxide, phosgene, morphine, etc., is well known (see Gassing, also Poisons and Antidotes). There are many other chemicals that are potential killers. The vapour of any volatile substance whatever is a potential suffocation hazard whether or not it is toxic.

There are three principal methods of ingress of chemicals into the human system, namely, mouth, nose, and skin, and to a lesser degree the eyes and ears. The chance of a person taking a toxic material by mouth can be accounted for mainly by carelessness or by accident (unintentional carelessness) since labelling is required in all over-the-counter sales and in industry the workers should be adequately educated about the health hazards of materials they handle. This should be the responsibility of both the employer and the employee. Most toxic materials that enter the body by way of the mouth are either solid or liquid. Respiratory hazards that enter through the nose are generally vapours or gases. In this connection any vapour can cause suffocation by cutting down the supply of oxygen required by the body and is a potential hazard. Ventilation is the best protection. Since most vapours are heavier than air special precaution should be made to ventilate the floor space as well as the ceiling. A positive supply of fresh air by forced circulation is better than depending upon natural draughts. Air should be supplied at a desired temperature, humidity, and cleanliness. Since dust and dryness are not only a health but hazardous in the matter of fires and explosions the use of air conditioning cannot be too strongly recommended and

Two factors are of prime importance in respiratory hazard, vapour pressure and solubility in the blood. Many of the vapours, 2, and gases have specific toxicity and special lists should be con-

these cases. It is especially recommended that employer, employee, physician, and welfare worker obtain for ready reference a list of the specific toxic chemicals that he is likely to meet in his work, and to know how to prevent, protect, and treat for the toxic material.

Many chemicals cause irritation to the skin. This irritation may cause a rash or remove oil from the skin causing it to become dry and crack. In either case the skin then becomes more susceptible to infection and should be protected. Chemicals that obtain ingress through the eyes and ears may cause injury to the optical and olfactory nerve. For example, wood alcohol and carbon disulphide affect the eye.

The systemic effects of exposure to chemicals may be acute or chronic. Benzene, for example, affects the blood. Chlorinated hydrocarbons affect some of the internal organs. The tissues of the nerves and heart are affected by other chemicals. The following types of chemicals present health hazards :

- (1) Petroleum hydrocarbons have mild anæsthetic and intoxicating effects.
- (2) Turpentine vapours cause headache, nausea, depression, and in some cases nephritis.
- (3) Benzol generally attacks the nervous system and the walls of the arteries, causing hæmorrhage.
- (4) Chlorinated hydrocarbons are strong anæsthetics, some cause dermatitis, some affect the liver and cause jaundice. They are toxic when inhaled, and when absorbed through the skin.
- (5) Alcohols are intoxicants.
- (6) Ethers are strong anæsthetics.
- (7) Ketones cause lowering of the blood pressure, and narcotic poisoning.

The specific effects of a given chemical will vary greatly with different individuals. It is advisable to ascertain in advance by a medical test the susceptibility of an individual to a given chemical before he is assigned to an operation where the chemical is used.

Preventive measures for health hazards should involve proper ventilation, instruction of the worker in the matter of safe practices, and furnishing of safety appliances. There should be a careful selection of a physician who is well acquainted with the potential health hazards of the chemicals employed.

It is important in the handling of all hazardous chemicals that emphasis on and instruction in safe practice be continuous, so that familiarity does not breed carelessness. Herein lies one of the most insidious dangers against which all interested parties should be ever watchful.

The regulations adopted (1950) a rigid code governing the handling and storage of chemicals to be administered by the Department of Fire. Chemicals are divided into six groups, as follows :

exposure to **liquids**, such as nitric acid, sulphuric acid, bromine, phosphorus trichloride, halogenated hydrocarbon liquids, caustic alkali that includes hydrofluoric acid.

**Oxidizing chemicals**, such as sodium chlorate, ammonium nitrate, potassium perchlorate, potassium chlorate.

**Dangerous gases**, such as boron trimethyl, hydrogen sulphide, carbon monoxide, nitrous oxide, chlorine, sulphur dioxide, helium, nitrogen, carbon dioxide.

**Flammable solids**, such as phosphorus, cellulose nitrate, magnesium powder, sodium, molten sulphur, quicklime.

**Explosives**, such as nitroglycerin, mercury fulminate, silver tartrate, TNT, picric acid, dynamite, black powder.

**Flammable liquids**, such as ethyl alcohol, benzene, acetone.

(See "A Digest of Laboratory Safety Practices," by James S. Sweely, in *Chem. Eng. News*, Dec. 26, 1949, p. 3861.)

*References*: *Fire Risks in Industry*, by A. Cameron (Institute of Chemistry); *Fire Prevention and Protection*, by Hutson (Spectator Co., New York); *Fire and Explosion Risks*, by Schwartz-Salter (C. Griffin and Co., London); *Static Electricity* (National Fire Protection Association, Boston); *Manual of Industrial Health Hazards*, by J. B. Ficklen (Service to Industry, West Hartford, Connecticut); *Industrial Toxicology*, by Alice Hamilton (Harper and Bros., New York); *Skin Hazards in American Industry*, U.S. Public Health Service Bull. No. 215; *Static Electricity in Nature and Industry*, U.S. Bureau of Mines Bull. No. 368; *Handbook of Fire Protection*, by Crosby, Fiske and Forster (D. Van Nostrand Co., New York); *The Manual of Industrial Safety*, by Williams (McGraw-Hill Book Co., New York); *Industrial Poisons in the United States*, by Alice Hamilton (Macmillan Co., New York); *Industrial Hygiene and Toxicology*, 2 vol., by Frank A. Patty, editor (Interscience Publishers, New York); *Sedgwick's Principles of Sanitary Science and Public Health* (Macmillan Co., New York and London); *Chemistry in Relation to Fire Risk and Fire Extinction*, by A. M. Cameron (Pitman and Sons, London); *NFPA Handbook of Fire Protection* (National Fire Protective Assn., Boston).

**HAZEL-NUT OIL** is reported to have a sp. gr. of about 0.9152 to 0.9156, sap. v. about 190, i.v. (Hanus) 84 to 85, and to be devoid of arachidic acid. The hazel (*Corylus*) is a genus of the N.O. Cupuliferæ, the common hazel being *C. Avellana*.

**HEALTH** — See Foods.

**HEAT (Thermochemical Aspects)** — The distinction between amount of heat and intensity of heat is fundamental in connection with the thermochemical aspects of reactions. Intensity of heat is the more familiar concept and is synonymous with temperature. Temperature and heat are sometimes loosely used interchangeably in the same way that weight and mass terms are confused. It is important to bear in mind when speaking of temperature correctly that it signifies *degree* or *intensity* of heat. The degree of temperature plays a very important role in many reactions. Some reactions take place on simple contact of materials at ordinary temperature, whereas others require more or less elevated temperature. Furthermore, careful regulation of the

temperature is demanded for the smooth progress of certain reactions, for example, the nitrating of cellulose. A comprehensive survey is contained in *Temperature—Its Measurement and Control in Science and Industry* (Reinhold Publishing Corp., New York).

For those reactions whose rate of change has been measured the approximate result has been found that an increase of temperature of about 10° C. (18° F.) doubles the rate of the reaction, thus cutting the time to one-half. What this means, even over a short range of temperature, can be vividly shown by examining the following table.

Temperature ° C.	Relative Rate compared to Rate at 20° C.	Time required As an Example
20	1	60 minutes
30	2 times	30 "
40	4 "	15 "
50	8 "	7.5 "
60	16 "	3.8 "
70	32 "	1.9 "
80	64 "	1.0 "

Thus, an increase of temperature of 60° C. (as from 20° to 80° C. in the above example) *decreases* the time for a reaction to proceed at the higher temperature to approximately 1/60th of the time required at the lower temperature (any other factors that might affect the rate are neglected).

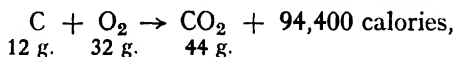
Very high temperatures are required for the successful operation of the iron blast-furnace reactions, for glass manufacture, as well as in the production of coke and coal gas, in the smelting of metals, and in the burning of clay for bricks (see Temperatures, below). A principal limitation in practice in these cases is the temperature resistance of the container (see Refractories).

The *amount of heat* involved in a given change, whether chemical or physical, is measured by the relatively small temperature rise—or fall—accurately measured of a relatively large amount of a reference substance, usually water (or ice). The product of this temperature rise—or fall—multiplied by the mass of reference substance multiplied by the specific heat of this substance gives the amount of heat change. The units of amount of heat in common use are *British Thermal Units* (B.Th.U.) where the temperature change is measured in degrees Fahrenheit and the water—or water equivalent—in pounds Avoirdupois, and *Calories* (Cal.) where the temperature change is in degrees Centigrade and the water—or water equivalent—in kilograms. The small calorie (cal.) is 1/1000th of the above large Calorie, the mass being expressed in grams instead of kilograms. One Calorie equals 3.96 British Thermal Units. The "rational" calorie is precisely defined as the amount of heat required to raise one gram of water from 0° to 100° C. at a pressure K.C.E.—17

of one atmosphere, and the "mean" calorie as 1/100th rational calorie. The mean calorie is almost the same as if the water were raised one degree from 15° to 16° C. The instrument used for measuring the amount of heat is called a *calorimeter*.

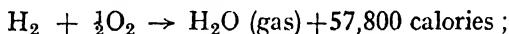
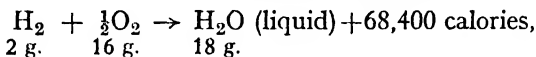
All chemical reactions involve the evolution or absorption of a definite amount of heat. This is a very important consideration, as the removal or supply of this amount of heat must be provided for, either intentionally or unintentionally.

Consider the burning of fuel, which is an important chemical reaction carried out for the purpose of producing heat. Here each fuel has its characteristic heating or fuel value, some illustrations being as follows :

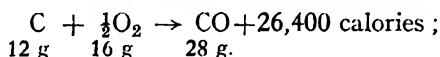


that is, 7,900 calories per one gram or 14,200 British Thermal Units per one pound of carbon burned to carbon dioxide.

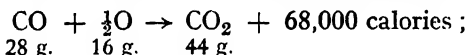
If hydrogen gas is burned to water then :



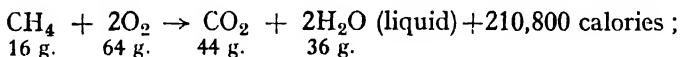
if carbon burned to carbon monoxide then :



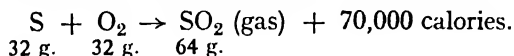
if carbon monoxide burned to carbon dioxide then :



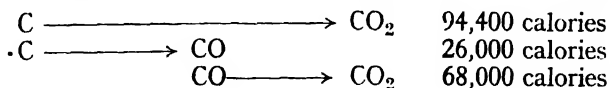
if methane gas burned to carbon dioxide and water (liquid) then :



if sulphur burned to sulphur dioxide then :



The first, third, and fourth examples above illustrate a thermochemical principle known as the *Law of Hess*, namely, that no matter what route a reaction follows the amount of heat for the complete route—same initial and same final materials—is the same, thus :



94,400 calories

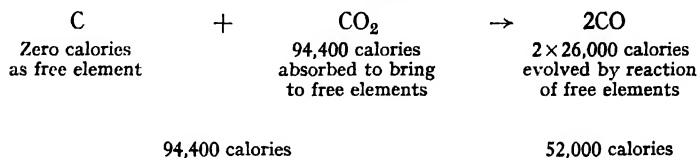
If all but one heat factor by two different routes is known this unknown factor may be ascertained arithmetically. In the example, the reaction

heat  $C \rightarrow CO$  is actually calculated by taking the difference between  $C \rightarrow CO_2$  and  $CO \rightarrow CO_2$ , both of which are readily obtained calorimetrically.

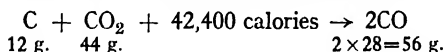
For further information related to this field see Explosive Range, Flash Points, and Ignition.

The **Heat of Formation** of many important chlorides, oxides, sulphides, and hydrides is tabulated under Elements. The heat content is zero for the free elements, usually under pressure of one atmosphere and temperature of  $25^\circ C$ .

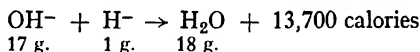
The heats of dissociation, of association, of transformation, of neutralization, of ionization, and of combustion are special cases of the **Heat of Reaction**. The heat of reaction can be calculated from a knowledge of the heats of formation of all substances concerned in a given reaction. Thus, for the reaction carbon plus carbon dioxide to form carbon monoxide, which reaction takes place readily at a temperature of approximately  $1,000^\circ C$ ., the result would be :



requiring that  $94,400 - 52,000 = 42,400$  calories more is absorbed than evolved, so that the thermochemical equation is :



For the reaction of neutralization the thermochemical equation is :



for highly ionized bases and acids. Variations from this value are attributed to heat of ionization of base or acid or both. (See Bichowsky and Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corp., New York) ; Parks and Huffman, *Free Energy of Some Organic Compounds* (Reinhold Publishing Corp., New York) ; Winslow and Herrington, *Temperature and Human Life* (Princeton University Press) ; Kharasch in *Bur. Standards J. Research*, **2**, 359 (1929) ; *International Critical Tables* (McGraw-Hill Book Co., New York) ; and Fuels.)

See Boiling Points, Cryoscopy, and Vapour Pressure.

The so-called **Heat of Solution** of soluble substances is referred to under Solution and Solvent Action ; and Anti-freezes.

**Temperatures** at which solid bodies melt are known as their **melting** or **fusing points** ; temperatures at which liquid bodies solidify or vaporize (at 760 mm. of mercury pressure) as their **freezing** and **boiling points**, respectively ; and temperatures at which vapours condense (at 760 mm. of mercury pressure) as their **condensation points**.

SOME NOTABLE TEMPERATURES AT ONE STANDARD ATMOSPHERE  
PRESSURE

\* Fundamental or primary fixed points used in defining the standard working scale of temperature according to The International Temperature Scale of 1948 (6 points cited).

† Secondary fixed points according to The International Temperature Scale of 1948 (22 points cited).

See Elements, and Oxides for other temperatures.

	Degrees Centigrade
Theoretical zero of temperature .. ..	—273·15
(U.S.A. custom —273·16)	
*Boiling point of oxygen (primary) .. ..	—182·970
†Carbon dioxide (Solid $\rightleftharpoons$ Vapour) .. ..	—78·5
†Freezing point of mercury .. ..	—38·87
*Melting point of ice (fundamental) .. ..	0·000
†Triple point of water (Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Vapour)	+0·0100
Mean atmospheric temperature .. ..	+15·5
†Sodium sulphate decahydrate—Sodium sulphate anhydrous—Water .. ..	32·38
Blood heat (human) .. ..	36·9
*Condensing point of steam (fundamental)	100·000
†Triple point of benzoic acid .. ..	122·36
†Condensing point of naphthalene .. ..	218·0
†Freezing point of tin .. ..	231·9
†Condensing point of benzophenone .. ..	305·9
†Freezing point of cadmium .. ..	320·9
†Freezing point of lead .. ..	327·3
†Boiling point of mercury .. ..	356·58
Pyrites burners .. ..	400–500
†Freezing point of zinc .. ..	419·5
*Condensing point of sulphur (primary) .. ..	444·600
Red heat just visible in the dark .. ..	526 (approx.)
†Freezing point of antimony .. ..	630·5
†Freezing-point of aluminium .. ..	660·1
Gas producers .. ..	900–1,300
Reverberatory furnaces .. ..	900–1,400
Kilns (for various burnings) .. ..	900–1,600
*Freezing point of silver (primary) .. ..	960·8
*Freezing point of gold (primary) .. ..	1,063·0
†Freezing point of copper (in reducing atmosphere) .. ..	1,083
Coke ovens (chambers) .. ..	1,100 (approx.)
Deep orange heat .. ..	1,100 (approx.)
Steel melting point .. ..	1,350 (approx.)
Glass-furnace heat .. ..	1,375 (approx.)
Frit kilns .. ..	1,100–1,400 (approx.)
White heat .. ..	1,500 (approx.)

				Degrees Centigrade
†Freezing point of nickel	..	..	..	1,453
†Freezing point of cobalt	..	..	..	1,492
Cast-iron melting point	..	..	..	1,530 (approx.)
†Freezing point of palladium	..	..	..	1,552
Open-hearth furnace..	..	..	..	1,600 (approx.)
†Freezing point of platinum	..	..	..	1,769
Blast-furnace heat	..	..	..	1,930 (approx.)
†Freezing point of rhodium	..	..	..	1,960
†Freezing point of iridium	..	..	..	2,443
Oxyhydrogen flame	..	..	..	2,800 (approx.)
Oxyacetylene flame	..	..	..	3,100-3,300
†Melting point of tungsten	..	..	..	3,380
Electric furnace	..	..	..	3,600 (approx.)
Arc lamp	..	..	..	4,000

Temperatures as measured from the theoretical zero  $-273^{\circ}\text{C.}$  are termed absolute temperatures and marked  $T$ , so that if  $t^{\circ}$  indicates the Centigrade or Celsius temperature  $T^{\circ}=273+t^{\circ}$ ; in other words, the Centigrade or Celsius absolute is made by adding 273 to the Centigrade or Celsius reading, and the Fahrenheit absolute by adding 460 to the Fahrenheit reading. The Centigrade or Celsius absolute scale is also called the Kelvin scale (degrees K).

Ordinary temperatures are usually determined in English-speaking countries according to two scales, but chemists for the most part use what is called the Centigrade or C. scale which is to be known henceforth, according to the recommendation of the International Union of Chemistry (1949), as the Celsius scale (degrees Celsius) in honour of its inventor, Anders Celsius, a Swedish astronomer; the other is known as the Fahrenheit or F. There is still another scale, known as the Réaumur or R., now practically obsolete. On the Centigrade scale the melting point of ice is regarded as zero ( $0^{\circ}$ ), and the boiling point of water is  $100^{\circ}$ ; whereas on the Fahrenheit scale the melting point is  $32^{\circ}$ , and the boiling point is  $212^{\circ}$ . To convert a Centigrade reading into a Fahrenheit reading, multiply by 1.8 and then add 32. To convert a Fahrenheit reading into a Centigrade reading, subtract 32, and divide by 1.8. In the Réaumur scale, the interval between the freezing and the boiling points of water is divided into  $80^{\circ}$  instead of  $100^{\circ}$ , as in the Centigrade scale, so that in this case, while the freezing point is  $0^{\circ}$ , the boiling point of water is  $80^{\circ}$ . (See *Temperature: Its Measurement and Control in Science and Industry* (Reinhold Publishing Corp., New York); Pyrometers, and Thermometers.)

**Low Temperatures** — By evaporating liquid hydrogen under reduced pressure, Dewar reached to a temperature  $260^{\circ}\text{C.}$  below freezing-point, that is, only  $13^{\circ}\text{C.}$  above absolute zero. The lower temperature of  $-271.5^{\circ}\text{C.}$ , or only  $1.6^{\circ}$  above absolute zero, was later brought about by the evaporation of liquid helium under very low pressure, and W. H. Keesom, of Leyden University, has since succeeded in reaching

and maintaining a temperature of 0.82 of a degree above absolute zero throughout a space of 200 c.c. Low temperatures are discussed by W. F. Giaque in the Chandler Medal Address on "Temperatures Below 1° Absolute" (*Ind. Eng. Chem.*, **28**, 743 (1936)). (See Helium.)

**Temperature Control**— Various appliances to control any temperatures between  $-200^{\circ}$  and  $+1,700^{\circ}$  C. are available, the control being either electrical or mechanical. See *Methods of Measuring Temperature*, by Ezer Griffiths (C. Griffin and Co., London); *Calculation of Heat Transmission*, by Fishenden and Saunders (H.M. Stationery Office).

#### HEATS OF FUSION AND MELTING-POINTS OF NOTABLE SUBSTANCES

Substance	Heat of Fusion Cal. per Gm.	Melting Point °C
Water .. .. .	79.7	0.00
Aluminium .. .. .	71	658.7
Sodium nitrate .. .. .	45.3	333
Acetic acid .. .. .	44.7	16.7
Copper .. .. .	43	1083
Ethylene glycol .. .. .	42	-12
Sodium hydroxide .. .. .	40	318
Benzene .. .. .	30	5.4
Phenol .. .. .	29	25.4
Zinc .. .. .	26	419
Nitrobenzene .. .. .	22	5.7
Aniline .. .. .	21	-7.0
Tin .. .. .	14	119
Lead .. .. .	11	327
Sulphur .. .. .	9	119
Mercury .. .. .	3	-39

The **Mechanical Equivalent of Heat** is expressed by the ascertained fact that a weight of 1 pound falling through 778 feet may produce, by friction or otherwise, enough heat to raise the temperature of 1 pound of water 1° F.

For **Flow of Heat** see Heat Transfer.

**Latent Heat**— When a gas, such as carbon dioxide, is liquefied by cooling and pressure and then allowed to escape by a jet from its container, some part of the escaping gas will absorb heat from the other part, causing it to be deposited in the solid form, resembling snow. In a similar way, snow when lying on the ground, during a thaw, will, by absorbing heat from its surroundings, cause ice to be produced in its immediate vicinity. (See Refrigeration.) In passing from the solid to the liquid state, there is what appears to be a disappearance of heat, so that when solid ice liquefies to water, the heat which thus disappears

through 79° C. This is termed latent *heat of fusion*. On the other hand, when water is frozen, the same amount of heat is evolved—latent *heat of solidification*, equal to and commonly expressed as *heat of fusion*.

A corresponding evolution of heat takes place when all substances pass from the liquid to the solid form, the amount varying with the particular substances. Thus, when a saturated solution of sodium sulphate is suddenly agitated, it at once crystallizes, and the thermometer will indicate an immediate rise of temperature. The amount of heat involved is known as *heat of crystallization*.

Again, heat is rendered latent when substances pass from the liquid to the gaseous state, as when, for example, water is converted into steam, the latent *heat of vaporization* of which is 540 thermal units. The reverse change of condensation of gas or vapour to liquid produces an equal but opposite heat change—*heat of condensation*, equal to and commonly expressed as *heat of vaporization*.

#### HEATS OF VAPORIZATION AND BOILING-POINTS OF NOTABLE SUBSTANCES

Pressure : 760 mm. of mercury

Substance	Heat of Vaporization Cal. per Gm.	Boiling Point °C
Water .. .. .	540	100.0
Ethyl alcohol .. .. .	204	78.3
Acetone .. .. .	124	56.1
Acetic acid .. .. .	97	118.3
Carbon disulphide .. .. .	84	46.3
Mercury .. .. .	65	357
Phosphorus trichloride .. .. .	51	78
Carbon tetrachloride .. .. .	46	76.8
Silicon tetrachloride .. .. .	36	57

**Specific Heats** — (See Elements for data for individual elements.)

It is a known fact that equal weights of different substances absorb different quantities of heat through the same range of temperature ; water, for example (which exhibits the highest thermal capacity of all known substances), requires thirty times the amount required by the same quantity of mercury to raise the temperature through a given number of degrees. These relative capacities furnish the so-called specific heats of substances, which may be defined as the ratios of their thermal capacities to that of an equal weight of water ; thus, the specific heat of water being taken as the unit, that of mercury is  $\frac{1}{30}$ , or 0.033. There is a definite relation between the specific heats and the atomic weights of various solid elements, the former being inversely proportional to the numbers known as their atomic weights. This law, known

as that of Dulong and Petit, is expressed by stating that the thermal capacities of atoms of the elements in the solid state are equal. Atomic heats are represented by multiplying the specific heats by the atomic weights. The solid elements of low atomic weight do not follow this regularity in every case.

The molecular heat of a compound is the sum of the atomic heats of its constituent elements.

**HEAT BALANCE** — A quantitative statement of all heat entering and leaving a piece of apparatus, or any part of it, in a given time. All the comments in the article Material Balance apply equally to heat balances if the word "heat" be substituted for "material."

**HEAT INSULATION** — See Heat Transfer.

**HEAT PUMP** — See Evaporation.

**HEAT TRANSFER** — The operation of heating or cooling materials, nearly always necessary at some stage in chemical manufacturing processes. The commonest industrial heating media are combustion gases and steam. Cooling may be effected by water, air, or, at low temperatures, by refrigerants. Heat exchange is a method of economizing heat by causing hot fluids (that require to be cooled) to transfer their heat to cold fluids (that are thereby heated).

Heat transfer utilizes the three physical processes of conduction, convection, and radiation. Conduction is the passage of heat through solid bodies, or through fluids in which there is no turbulence. Convection is the transfer of heat through a fluid (liquid or gas) by turbulent motion, whereby portions of heated fluid are carried bodily to colder regions and *vice versa*. In radiation, heat is transferred from one body to another by electromagnetic waves.

For the purposes of calculation, the rate of heat transfer by conduction and convection is treated as being proportional to a driving force, namely, the temperature difference, multiplied by a thermal conductance. This is not strictly correct, since the conductance itself varies somewhat with temperature, but over a moderate range of temperature it may often be taken as constant. Thermal conductance per unit area is expressed as a heat transfer coefficient, common units being B.Th.U. per square foot per degree Fahrenheit per hour, or calories per square centimetre per degree Centigrade per second. The general equation for heat transfer by conduction and convection is:  $H = SU\theta$ , where  $H$  = total quantity of heat transferred in unit time,  $S$  = heat transfer surface,  $U$  = overall heat transfer coefficient,  $\theta$  = temperature difference.

The reciprocal of the heat transfer coefficient is the thermal resistance per unit area. Usually there are several resistances in series. For example, when heat is transferred from combustion gases through a steel tube to water, there are at least three heat transfer coefficients involved, namely, for the gas side,  $h_g$ ; for the tube itself,  $h_t$ ; and for

the water side,  $h_w$ . The overall heat transfer coefficient is the reciprocal of the overall resistance, which is the sum of the individual resistances, *i.e.* :

$$\frac{1}{U} = \frac{1}{h_g} + \frac{1}{h_t} + \frac{1}{h_w}$$

$h_t$  is equal to the thermal conductivity of steel divided by the thickness of the tube wall. On the gas side, the principal resistance to heat transfer is the stagnant film of gas adhering to the outer surface of the tube, and a similar film of water obstructs heat transfer inside the tube (see Fluid Dynamics).  $h_g$  and  $h_w$  are therefore called film coefficients. The thinner the stagnant film, the higher the film coefficient; since film thickness varies inversely as the 0.8th power of the fluid velocity,  $h_g$  and  $h_w$  are directly proportional to the 0.8th power of the gas and water velocities respectively. Formulae for calculating film coefficients under various conditions will be found in the textbooks referred to at the end of the article. For the common case of liquids or gases flowing inside pipes, the film coefficient is given by the McAdams equation :

$$\frac{hD}{k} = 0.0225 \left( \frac{DV\rho}{\mu} \right)^{0.8} \left( \frac{c_p\mu}{k} \right)^{0.4}$$

where  $h$  = film coefficient,  $D$  = inside diameter of pipe,  $k$  = thermal conductivity of fluid,  $V$  = fluid velocity,  $\rho$  = fluid density,  $\mu$  = fluid viscosity at flowing temperature,  $c_p$  = specific heat of fluid at constant pressure, all in consistent units (*e.g.*, foot-pound-hour, or centimetre-gram-second).

For liquids which foul the heat transfer surface by depositing scale, etc., a fouling coefficient  $h_f$  must be introduced to allow for the additional resistance to heat transfer. The thermal resistance due to fouling is sometimes expressed as a "fouling factor,"  $\frac{1,000}{h_f}$ .

In radiation the heat transfer coefficient concept is inappropriate because the rate of heat transfer is not proportional to the temperature difference, but to the difference between the fourth powers of the absolute temperatures of the two bodies between which heat is being transferred (the Stefan-Boltzmann law). It is also proportional to the emissivity and absorptivity of the hot and cold surfaces respectively. Dull black surfaces have the highest emissivity and absorptivity, polished metal surfaces, the lowest. Gases at high temperatures also radiate heat, especially water vapour and carbon dioxide. Radiation from combustion gases has to be taken into account in furnace calculations.

*References* : Standard works listed under Chemical Engineering ; W. H. McAdams, *Heat Transmission* (McGraw-Hill Book Co., New York) ; H. L. Stoever, *Applied Heat Transmission* (McGraw-Hill Book Co., New York) ; M. Fishenden and O. A. Saunders, *Introduction to Heat Transfer* (Oxford University Press).

## Some Heat Conducting Materials

## Some Heat Insulating Materials

Material	Thermal Conductivity*	Material	Thermal Conductivity *
Silver .. ..	1.10	Hair, horse .. ..	0.00012
Copper .. ..	0.92	Cork .. ..	0.00013
Aluminium .. ..	0.46	Wood dust .. ..	0.00014
Magnesium .. ..	0.38	Asbestos paper .. ..	0.00035
Zinc .. ..	0.27	Rubber, soft .. ..	0.00044
Brass .. ..	0.23	Plaster .. ..	0.0007
Tin .. ..	0.15	Cement, Portland .. ..	0.0007
Nickel .. ..	0.14	Sand .. ..	0.0009
Graphite .. ..	0.10	Brick, fire .. ..	0.0011
Iron (steel) .. ..	0.10	Glass .. ..	0.0017
Lead .. ..	0.08	Rock wool .. ..	0.0020
		Magnesia, brick .. ..	0.0027
		Carbon, gas .. ..	0.0085

\* Thermal conductivity is expressed in gram-calories transmitted at 0° C. per second through a plate 1 centimetre thick and 1 square centimetre in area when the temperature difference between the sides of the plate is 1 degree Centigrade. For British Thermal Units per second/inch/square inch/degree Fahrenheit multiply the values by 0.0056.

**HEAT TRANSMISSION** — Usually synonymous with Heat Transfer (see same). In England it has been suggested that the term "Heat Transmission" should be reserved for the conveyance of heat to a point remote from its place of generation by a circulating heating medium such as water, oil, or steam. Some distinction between the two terms might indeed be useful, but it is not generally made.

**HEAVY HYDROGEN** — See Hydrogen (Heavy).

**HEAVY SPAR (Barytes)** — Mineral barium sulphate ( $\text{BaSO}_4$ ), crystal system No. 4, and sp. gr. 4.3 to 4.7.

**HEAVY WATER** — See Hydrogen (Heavy.)

**HECTARE** — See Weights and Measures.

**HECTO** — Prefix signifying "a hundred of" in the metric system.

**HEDEOMA OIL (American Pennyroyal Oil)** — A volatile oil distilled from *Hedeoma pulegioides* in North Carolina, Ohio, and Tennessee; sp. gr. 0.925 to 0.940; opt. rot. +18° to +35°; soluble in 2 volumes of alcohol (70 per cent.); distinct from European pennyroyal oil. (See Pennyroyal Oil.)

**hederin** ( $\text{C}_{41}\text{H}_{64}\text{O}_{11}$ ) — A glycoside contained in ivy leaves and seeds (*Hedera helix* of N.O. Araliaceæ), which yields upon hydrolysis an acid named hederagenin, together with *l*-arabinose and rhamnose.

**HEHNER VALUE** — See Fats.

“ **HELIARC** ” **WELDING** — The tungsten arc process employing originally a helium gas protective shield over the weld puddle. Argon has since been substituted for the helium because of better performance. Mixtures of several inert gases are also receiving some attention. The process was originally developed for the fluxless welding of magnesium but has been extended to aluminium, copper, iron, nickel, and silver alloys.

**HELIOTROPIN** — See Piperonal.

**HELIUM** (He) — Atomic weight, 4.003. See Elements for other data.

Helium is a colourless gas, next to hydrogen in lightness, being twice as heavy as the latter ; previously known as a constituent of the sun's atmosphere, but much more recently recognized as present in the air in extremely minute quantity (4 volumes in 1,000,000), in some natural gases, in certain mineral spring waters, notably those of Bath. It is also found in association with a large number of mineral compounds of uranium, thorium, and other rare earths, including *cleveite*, *bröggerite*, and *uraninite* (*pitch-blende*), and can be obtained from monazite sand, as also from the helium-neon mixture which results as a by-product in the separation of oxygen and nitrogen from liquefied air. The helium content of Travancore monazite sand is of the order of 1 c.c. per gm. Helium in uranium and thorium ores arises from the radioactive decay of these elements and their families, since the alpha particle is the helium nucleus. In common with the other members of the argon group, helium is very inert and practically devoid of chemical characters. Glass is said to be appreciably permeable to helium, while palladium is almost completely impermeable.

Certain wells of natural gas in many parts of the world contain small proportions of helium ; the gas in certain Alberta fields contains from 0.38 to 0.50 per cent. ; some in Kansas from 0.5 to 2 per cent., and others in Colorado and Texas from 1 to 8 per cent. From such sources it is produced in large quantities as a government undertaking in the United States. In the matter of inflating balloons and dirigible airships it has the advantages over hydrogen that it diffuses more slowly, is non-inflammable and non-explosive in admixture with air, and the disadvantages that it is much more costly, is subject to governmental regulation, and exhibits only 92.6 per cent. of the lifting power of hydrogen. According to Snyder and Bottoms its thermal conductivity is nearly six times that of air and for airship work its greater density than hydrogen is offset by the diffusion of the last-named gas being 50 per cent. more rapid, etc. It also promises to be of value in replacing the nitrogen of air used by divers, as helium is less soluble in blood than is nitrogen, so that the pressure on the operator may be relieved more quickly without danger of contracting the “ bends ” in the joints caused by gas escaping from the blood. There is a natural gas-supply at Alberta from which it has been found practicable to isolate helium of 97 per cent. purity on a commercial scale at a cost of less than 2½d. per cubic foot. The gas is stated to be now obtainable in one direct operation, whereas in the older process the natural

gas was subjected to a liquefying process and the methane content separated first, then the other constituents, the helium with its low liquefying point remaining to the last.

The crude gas can be purified by passage over heated copper oxide to remove the hydrogen and hydrocarbons, and then passed over metallic magnesium heated to  $600^{\circ}\text{C.}$  to free it from nitrogen, and finally over metallic calcium at  $560^{\circ}\text{C.}$ , thus yielding helium of 99.5 per cent. purity.

Helium liquefies at  $-269^{\circ}\text{C.}$ , and by subjecting the liquid to a pressure of 128 atmospheres and a temperature of  $4\frac{1}{4}^{\circ}\text{C.}$  absolute, Keesom, in 1926, at Leyden University, succeeded in solidifying helium.

At the temperature of liquid helium,  $4.3^{\circ}\text{K.}$ , certain metals, for example, mercury, tin, and lead, become superconductors of electricity, losing all measurable resistance to the flow of current, and sheets of such metals become effective screens against magnetism. Niobium reaches the superconductivity state at the astonishingly high temperature of  $9.2^{\circ}\text{K.}$  Other superconductors besides the metals mentioned are aluminium, zinc, cadmium, gallium, titanium, vanadium, and thorium.

When the temperature of liquid helium is lowered to  $2.19^{\circ}\text{K.}$  it ceases to boil. The lowering is accomplished by connecting the interior of the insulated container with a vacuum, and as helium vapour passes off the remaining liquid becomes colder and colder until the temperature of the liquid helium reaches  $2.19^{\circ}\text{K.}$  At this temperature the surface of helium remains perfectly smooth; vapour still escapes but without any visible change at its surface. This is called helium II.

In contrast to liquids, which are characterized by viscosity, helium II has no viscosity as it flows through the tiniest openings. In contrast to gases, which are characterized by completely filling a container, helium II responds to gravity as does a liquid. It remains at the bottom of its container, and it forms a surface which seeks its own level. In contrast to solids, which are characterized by rigidity of structure, helium II flows through the tiniest of openings. Physicists call helium II a fourth state of matter, not gas, liquid, nor solid. There is also known solid helium obtainable at high pressure.

This state of matter possesses the hitherto unknown properties of :

- (1) *Creeping film.* When the bottom of a tiny open vessel is placed in helium II, the helium climbs up the side of the vessel and fills it to the same level as the exterior surface of helium, and if the vessel is then lifted slightly the helium goes back over the edge to the level of the exterior surface, without the aid of a siphon as water would require.
- (2) *Fountain effect.* When a vessel with fine tubes at top and bottom is lowered into helium II, the latter enters the bottom tube as would be expected, *but* when the vessel is warmed by light the helium passes through the top tube in a fountain.
- (3) *Second sound.* When one end of a vessel containing helium II is warmed, a pulse of heat passes rapidly through the vessel. This discovery was made by Russian

scientists about 1944, and has been confirmed by others. (4) *Inertia loss*. When a vessel containing helium II is rotated and its inertia measured as the temperature drops, the resistance to acceleration rapidly decreases at and below  $2.19^{\circ}\text{K}$ . It seems that some of the helium II "does not take part in the rotary motion but glides through the interpenetrating atmosphere of normal helium atoms without friction."

See "Low Temperature Physics," by Harry M. Davis (*Scientific American*, June, 1949, 30); "Temperatures Below One Degree Absolute," by Giauque (*Ind. Eng. Chem.*, 28, 743 (1936); *Helium*, by W. H. Keesom (Elsevier Publishing Co., New York and London); Atoms, Elements, Heat, Radioactivity, and Radium.)

**HELLEBORE** — Two plant products bear this common name: the roots of *Helleborus niger* or *H. viridis*, which are used in medicine, and the roots of *Veratrum album* or *V. viride*, which are used as insecticides. *H. niger*, sometimes called black hellebore or Christmas rose, contains the alkaloids helleborein and helleborin, which have some anæsthetic action. The *Veratrum* species (white, green, or American hellebore) contain a number of alkaloids including jervine, veratridine, and others. The *Veratrum* species are no longer widely used as insecticides. *Adonis vernalis* is sometimes called false hellebore. (See Delphinium, and *Veratrum*.)

**HEMATIN** — See Hæmatin.

**HEMATINE** — See Logwood Extract.

**HEMATITE (Hæmatite)** — See Iron.

**HEMICELLULOSES** — The hemicelluloses are regarded as natural polysaccharides of lower molecular weight and of less definite composition than cellulose. They are insoluble in water, and more readily hydrolysed by dilute mineral acids than is cellulose, so that they are more readily made available as food in the digestive tracts of herbivorous animals. In a report to the Medical Research Council on food values, Dr. McChance groups hemicelluloses as comprising profurfurals (including the pentosans, free pentose sugars, true hemicelluloses and pectins, nucleic acid, and the precursors of methylfurfural), inulin and the fructosans, and other hexosans such as mannans and galactans. (See Hexosans, Pentosans, and Pentoses.)

**HEMLOCK FRUIT** — The dried unripe fruits of *Conium maculatum*, an umbelliferous plant growing in Great Britain, Europe, Asia, North America, and Chili and containing the poisonous alkaloid, coniine,  $\text{C}_8\text{H}_{10}\text{N}(\text{C}_3\text{H}_7)$ . Coniine is a colourless oily liquid; b.p.  $167^{\circ}\text{C}$ ; soluble in alcohol and ether; sparingly soluble in water; it possesses a narcotic action similar to that of nicotine and is now seldom used in medicine. The alkaloid is obtained by distilling the crushed seeds with dilute alkali and extraction from the distillate. The natural alkaloid is dextro-rotatory whilst coniine obtained by synthesis is a racemic mixture. Hemlock leaves also contain coniine.

**HEMLOCK SPRUCE** — The dried inner bark of *Tsuga canadensis*, a tree commonly growing in Canadian forests. The bark contains from 10 to 14 per cent. of tannin and is principally used as a tanning material. The leaves and twigs of the same tree yield, on distillation, a volatile oil having a specific gravity of about 0.913 and which is soluble in alcohol and ether.

**HEMP and HEMPSEED OIL** — Hemp is cultivated for its fibre in many parts of Europe and elsewhere, and the seeds are extensively used as bird food. Many varieties of so-called hemp, such as those from Bombay, Madras, Jubbulpore, and Sann, are stated to be really pseudo-hempes derived from *Crotalaria juncea*, although it is difficult to distinguish them from genuine hemp which is obtained from *Cannabis sativa* (Indian Hemp). Other varieties are the so-called Manilla and Sisal hempes. The ash of the genuine hemp contains about 2 to 6 per cent. ferric oxide, whilst that of the pseudo varieties contains from 8 to 12 per cent.

The oil obtained by pressure or extraction from hempseed is of faint green colour, non-drying in character and turns brownish-yellow upon standing. It solidifies at  $-27^{\circ}\text{C}.$ ; sp. gr. 0.925 to 0.928; sap. v. about 192.5; i.v. 141 to 148; ref. ind. 1.448 at  $15^{\circ}\text{C}.$  It is soluble in ether, benzene, and carbon disulphide and is used in the manufacture of soft soaps, paints, and varnishes.

Manchurian hempseed cake is stated to contain nearly 10 per cent. of oil, 30 per cent. of protein, 20 per cent. digestible carbohydrate, and to have considerable value as a feeding stuff. The tow is used as a cleaning waste and by upholsterers for stuffing. (See Cannabis.)

**HENBANE** — See Hyoscyamus.

**HENNA** — The powdered, dried leaves of *Lawsonia alba*, *L. inermis* and *L. spinosa*, which grow in North Africa, Arabia, Persia, and Ceylon. It contains about 1 per cent. of lawsone (2-hydroxy-1,4-naphthaquinone) which is an orange-yellow colouring matter melting at about  $192^{\circ}\text{C}.$ ; soluble in water, alkaline solutions, alcohol, and glycerin; insoluble in ether and in acid solutions. Henna is used as a hair-dye and, in the East, to dye the nails, teeth, and garments.

**HEPARIN** — A sterile preparation consisting of the sodium salt of a complex organic acid which is obtained from mammalian lung or liver tissue and which delays the clotting of shed blood. It consists of a polysulphuric ester of mucoitin of variable composition and its presence in the tissue mast cells was first demonstrated by Jorpes in 1933 (see *Heparin*, Oxford University Press).

In the preparation of heparin, minced lung or liver tissue is first extracted with a solution of sodium hydroxide and ammonium sulphate at  $50^{\circ}\text{C}.$  for one hour. After heating to  $70^{\circ}\text{C}.$ , the residual tissue is removed by filtration and dilute sulphuric acid added to the filtrate to adjust the reaction to pH 2.5. The precipitate is collected, washed with water, defatted, dried with alcohol, and subjected to trypsin-digestion at pH 8 and  $37^{\circ}\text{C}.$  for thirty-six hours. The reaction is then adjusted to pH 6 and crude heparin precipitated by the addition of

67 per cent. of ethyl alcohol. The crude heparin is purified by dissolving in water, made alkaline with sodium hydroxide, adjusting the reaction to pH 5 by the addition of acetic acid and precipitating protein by adding a 10 per cent. solution of cadmium chloride. The unwanted protein is removed by filtration and heparin is precipitated by adding acetone; excess cadmium is removed by dissolving the heparin in water, made slightly alkaline with sodium hydroxide and adding a solution of ammonium carbonate. The cadmium carbonate is removed by filtration and heparin re-precipitated from the filtrate by addition of acetic acid and acetone. It is further purified by precipitation as the benzidine or brucine complex, regeneration with ammonia, and crystallization as the barium salt in the presence of barium acetate and acetic acid. The barium salt is decomposed with sodium carbonate, barium carbonate removed by filtration, and the sodium salt precipitated from the filtrate by the addition of alcohol, washed with alcohol (95 per cent.) and then with ether and finally dried and powdered. (See O. Snellman *et al.* (*Nature*, London, **161**, 639 (1948)).)

Heparin is standardized biologically by comparing the concentration required to prevent the clotting of shed blood with the concentration of a Standard Preparation of Heparin necessary to produce the same effect. In Great Britain, the Standard Preparation is a sample of the dried sodium salt prepared from the crystallized barium salt of ox heparin; the international unit is the specific anticoagulant activity contained in 0.0077 mg. of the Standard Preparation (1947). Formerly, the activity of heparin was expressed in Toronto units. One Toronto unit was defined as the activity of 0.009 mg. of pure heparin sodium salt. (See Mangieri (*J. Lab. Clin. Med.*, **32**, 901 (1947)).)

For use in medicine, heparin is dissolved in a sterile solution containing 0.9 per cent. of sodium chloride (Normal Saline), solutions containing 5,000 units in 1 millilitre being the most commonly used. It is completely water-soluble and forms a clear, colourless, or faintly yellow solution. It should be stored at temperatures not exceeding 20° C., under which conditions it retains its potency for 12 months. It is used for the treatment of conditions in which it is desirable to delay or prevent the clotting of blood, such as coronary and cerebral thrombosis, blood transfusions, vascular surgery, and in the prevention of post-operative pulmonary embolism. For an account of the clinical uses of heparin, see D'Alessandro (*Surg. Gynec. Obstet.*, **74**, 62 (1942)); and for a review of anti-coagulants, MacIntosh (*J. Pharm. et Pharmacol.*, **6**, 353 (1949)).

'**HEPTALGIN** " (Phenadoxone) — A synthetic analgesic drug, being the hydrochloride of 4,4-diphenyl-6-morpholinoheptan-3-one.' It is stated to have a potency 6 times that of morphine, 20 times that of pethidine, and 3 times that of amidone. By the Dangerous Drugs Act (Application) Order 1950 (S.I. No. 52) Phenadoxone has been scheduled as a Dangerous Drug. The pharmacology of "Heptalgin" is described by B. Basil, N. D. Edge, and G. F. Somers, *Brit. J. Pharmacol.*, **5**, 125 (1950). (See Amidone, and Pethidine.)

**HEPTANE** — See Hydrocarbons.

**HEPTANOIC ALDEHYDE, Normal (Ænanthole)** ( $C_8H_{18}.CHO$ ) — A volatile, colourless liquid, sp. gr. 0.850, b.p.  $155^{\circ}C$ . Prepared by the dry distillation of castor oil under reduced pressure.

**HEPTOIC ACID (Ænanthic Acid)** ( $CH_3(CH_2)_6COOH$ ) — One of the normal fatty acids, m.p.  $-10^{\circ}C$ ., b.p.  $224^{\circ}C$ ., and sp. gr. 0.922; prepared by the oxidation of heptanoic aldehyde.

**HEPTYL** — The alkyl radical  $C_7H_{15}$ .

**HEPTYLENE** — See Hydrocarbons (Olefines).

**HERBICIDES** — Substances used to destroy plants, commonly called "weed killers." Many materials have been used for this purpose, including the non-selective herbicides such as sodium chlorate, sodium arsenite, ammonium thiocyanate, sulphuric acid, copper sulphate, petroleum and tar oils, and organic nitro compounds ("Sinox," "Elgetol," etc.).

Selective herbicides have been developed. Of these, 2,4-dichlorophenoxyacetic acid ( $Cl_2C_6H_3OCH_2COOH$ ) (2,4-D) has proved to be highly effective against broad-leaved plants. It is relatively harmless to monocotyledonous plants, however, and may thus be used to eradicate weeds in lawns, pastures, and other grass plantations without injuring the grass itself. This selective action of 2,4-D makes it valuable in other branches of agriculture, for example, in the growing of sugar-cane, corn, and rice, all of which are not appreciably affected by the chemical. Isopropyl phenyl carbamate (IPC), on the other hand, has been found to kill some grass species selectively without injury to broad-leaved plants.

**HERMETICAL SEAL** — The closure of a hollow vessel by melting or cementing the lips of its orifice or opening. Thermometers are hermetically sealed.

**HEROIN** — See Diamorphine.

**HERRING OIL** — See Fish Oils.

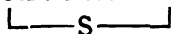
**HESPERIDENE** — A terpene constituent of oil of orange. (See Essential Oils, and Hydrocarbons (Terpenes).)

**HESPERIDIN** — See Glycosides.

**HETEROCYCLIC** — A division of organic compounds containing rings or nuclei of hetero-atoms; that is to say, one or more atoms of other elements than carbon in the ring, such as nitrogen, oxygen, or sulphur. Examples are pyridine ( $CHCHCHCHCH$ ), coumarone ( $C_6H_4CH:CH$ ),



and thiophene ( $CH:CH.CH:CH$ ). (See Resonance.)



**HEUSLER ALLOYS** — A range of non-ferrous alloys which are ferromagnetic. The original alloys contained copper, manganese, and tin with a maximum magnetizability at the composition  $\text{Cu}_2\text{MnSn}$ . The copper may be replaced by silver and the tin by aluminium, arsenic, antimony, bismuth, or boron without destroying the ferromagnetic nature of the alloys. (See article by L. A. Carapella and R. R. Hultgren in *Trans. Am. Soc. Mech. Engrs.*, **147**, 232 (1942).)

**HEXACHLOROCYCLOHEXANE** — See "Gammexane."

**HEXACHLOROETHANE (Perchloroethane, Carbon Trichloride)** ( $\text{C}_2\text{Cl}_6$ ) — A colourless crystalline compound of camphor-like odour; melts and sublimates at  $185^\circ\text{C}$ .; of specific gravity 2.09; soluble in alcohol and in ether; prepared by the action of chlorine on tetrachloroethylene ( $\text{C}_2\text{Cl}_4$ ). (See Acetylene, and Solvents.)

**HEXAETHYL TETRAPHOSPHATE** — See Tetraethyl Pyrophosphate.

**"HEXALIN" (Cyclohexanol)** ( $\text{C}_6\text{H}_{11}\text{OH}$ ) — A colourless liquid of sp. gr. 0.962, m.p.  $-24^\circ\text{C}$ ., and b.p.  $161.5^\circ\text{C}$ . It is prepared from phenol by hydrogenation in presence of nickel at  $180^\circ\text{C}$ ., and used for diminishing the hydrolysis of soap solutions, etc. Cyclohexanol is oxidized catalytically to make adipic anhydride which latter substance enters into the manufacture of nylon. There are several so-called hexalin and methylhexalin soaps on the market named "Savonade," "Texapon," "Texalin," "Hydralin," etc. They are alleged to possess the property of readily dissolving lime and magnesia soaps, to exhibit energetic washing action and excellent solubility, while being also stable to dilute organic acids. (See also "Sextol," "Sextate," "Sextone," and Hydrogenated Phenols.)

**HEXAMINE (Hexamethylenetetramine, Methenamine, "Urotropine")** ( $(\text{CH}_2)_6\text{N}_4$ ) — A white, crystalline substance prepared by the action of ammonia on formaldehyde; soluble in alcohol and in water; on heating, it sublimes, without melting, at about  $263^\circ\text{C}$ . It is used in medicine as a urinary antiseptic, and in industry as an accelerator in the manufacture of rubber.

**HEXANE** — See Hydrocarbons.

**"HEXAZOL"** — See Leptazol.

**HEXOBARBITONE ("Evipan")** ( $\text{C}_{12}\text{H}_{16}\text{O}_3\text{N}_2$ ) — A colourless, crystalline powder, namely, 5- $\Delta^1$ -cyclohexenyl-5-methyl-N-methylbarbituric acid; slightly soluble in water; soluble in alcohol, ether, and chloroform; m.p.  $145^\circ$  to  $147^\circ\text{C}$ . It is used as a hypnotic and sedative.

**HEXOBARBITONE SODIUM ("Evipan Sodium," "Hexanastab")** ( $\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}_2\text{Na}$ ) — A white, hygroscopic powder, being the monosodium derivative of hexobarbitone; very soluble in water, alcohol, and acetone; slightly soluble in ether and chloroform. It is administered as a 10 per cent. sterile solution by intravenous injection as an anæsthetic and was the first of the soluble barbiturate compounds to be used for this purpose, but has been replaced by safer compounds.

## 530 HEXÆSTROL — HIGH TEMPERATURE HEATING

**HEXÆSTROL** ( $C_{18}H_{22}O_2$ ) — A colourless, odourless, crystalline powder, namely, *meso-γδ*-bis-(4-hydroxyphenyl)-*n*-hexane, prepared by the catalytic hydrogenation of the dimethylether of diethylstilbæstrol and subsequent demethylation; insoluble in water; soluble in alcohol, acetone, and ether; slightly soluble in chloroform; m.p.  $185^\circ$  to  $188^\circ$  C. It is a member of the orally active æstrogenic compounds which have a physiological effect similar to the female hormone, æstradiol. Its synthesis and properties were first described by Campbell, Dodds, and Lawson, *Nature*, **142**, 1121 (1938); and Dodds *et al.*, *Proc. Roy. Soc.*, **B.127**, 140 (1939). It is considered to be nearly as potent as but less toxic than stilbæstrol. It is used in medicine for the treatment of a variety of conditions due to deficiency of the female hormone, æstradiol, and for inhibition of lactation in pregnancy. (See review of synthetic æstrogens by E. C. Dodds, in *J. Pharm. et Pharmacol.*, **3**, 137 (1949); Æstradiol, and Stilbæstrol.)

**HEXOSANS (Hemicelluloses)** — Derived from the hexoses having the general formula  $(C_6H_{10}O_5)_n$ , being condensation products of hexose sugars intermediate between simple sugars and the celluloses.

**HEXOSES** — A group of carbohydrates, most of them having the formula  $C_6H_{12}O_6$ . They fall chemically into two classes, the aldo-hexoses, including glucose (dextrose) and mannose having some of the properties of aldehydes, and the keto-hexoses, including fructose (lævulose), having some of the properties of ketones. (See Dextrose, and Fructose.)

**HEXYLENE** — See Hydrocarbons (Olefines).

**HEXYLRESORCINOL** ("Caprokol") — A white crystalline compound,  $\text{HO} \begin{array}{c} \text{OH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \end{array} \text{C}_6\text{H}_{13}$ , namely, 1,3-dihydroxy-4-*n*-hexylbenzene, having a pungent odour and astringent taste; slightly soluble in water, soluble in alcohol and ether; m.p.  $66^\circ$  to  $68^\circ$  C. Used in medicine as a urinary antiseptic.

**HIBISCUS OIL** (*Hibiscus cannabinus* L., a genus of the N.O. Malvaceæ) — The plant which yields this oil (known as the Deccan hemp of western India) is indigenous in Africa and cultivated in Java, yielding a fibre like jute. The seeds, known in Nigeria as "rama," contain about 20 per cent. fat, and can be used as cattle food. The sp. gr. of the oil is 0.9091, sap. v. 189.2, and i.v. 89.7; its chemical properties approximate those of ground-nut oil.

**HIDE POWDER** — See Tannins.

**HIDES** — See Tanning.

**HIGH-BOILING TAR ACIDS** — See Phenoloids.

**HIGH PRESSURE** — See Pressure (High).

**HIGH TEMPERATURE HEATING** — See Heat, and Pyrometers.

**HIPPURIC ACID (Benzoyl Glycine)** ( $C_6H_5CO.NH.CH_2.COOH$ ) — A constituent of the urine of horses, being the form in which benzoic acid is rendered harmless in the body. White crystals of m.p.  $187^\circ C.$ , readily soluble in alcohol and hot water. It is of great use in synthetic chemistry for the conversion of aldehydes into alpha-amino-acids (azlactone synthesis.)

**HISTAMINE (Iminazylethylamine)**  $\left( \begin{array}{c} HC = C.CH_2.CH_2NH_2 \\ | \quad | \\ HN \quad N \\ \diagdown \quad / \\ CH \end{array} \right)$  — Hista-

mine is formed from histidine by heating with an inorganic acid or by the action of bacteria. It has been synthesized; m.p.  $83^\circ C.$ , b.p.  $209$  to  $210^\circ C.$  It reduces blood pressure and stimulates gastric secretion. (See Anti-Histamines.)

**HISTAMINE ACID PHOSPHATE (Histamine Phosphate)** ( $C_5H_9N_3, 2H_3PO_4$ ) — A white crystalline solid, being the di-acid phosphate of 4- $\beta$ -aminoethylglyoxaline (histamine) obtained synthetically or from natural sources; soluble in water, slightly soluble in alcohol; m.p.  $130^\circ$  to  $133^\circ C.$  after sintering at about  $127^\circ C.$  It is used in medicine as a local vasodilator and to stimulate the gastric secretion in a diagnostic test for pernicious anaemia. (See Ergot.)

**HISTIDINE** ( $C_6H_9O_2N_3$ ) — An amino-acid, namely,  $\alpha$ -amino- $\beta$ -iminazole-propionic acid, obtained from the hydrolysis of proteins. It can be used for the preparation of histamine.

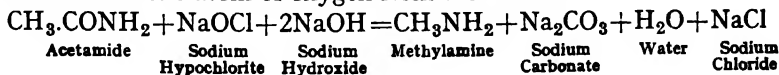
**HISTONES** — A certain class of proteins precipitable from solution by ammonia.

**HISTORICAL ASPECTS (See Elements for data for individual elements)** — See *Historical Introduction to Chemistry*, by T. M. Lowry (Macmillan Co.); *The Discovery of the Elements*, by Mary Elvira Weeks (Journal of Chemical Education, Easton, Pennsylvania); *Famous Chemists*, by Sir William A. Tilden (George Routledge and Sons, Ltd., London); *Eminent Chemists of Our Time*, by Benjamin Harrow (D. Van Nostrand Co., New York); *Van Nostrand's Scientific Encyclopedia* (D. Van Nostrand Co., New York); and *Journal of Chemical Education* (Easton, Pennsylvania).

**HISTOZYME (Aminoacylase)** — A ferment or enzyme occurring in the kidneys of pigs, calves, and horses, and the skeleton muscles of dogs (as also in some other organs), capable of hydrolysing hippuric acid with production of benzoic acid and glycine, etc.

**HOECHST 10820** — See Amidone.

**HOFMANN'S REACTION** is one for the formation of amines from amides by the use of bromine or chlorine in alkaline solution, that is, hypobromite or hypochlorite. The net result is the elimination of one atom of carbon and one atom of oxygen from the amide.



**HOLLANDS** — A gin-like spirit made from grain, rye being favoured.

**HOLMIUM** (Ho) — Atomic weight, 164·94. See Elements for other data.

A very rare element of the yttrium group of the rare-earth elements, occurring in the minerals *thulium*, *gadolinite*, *samaraskite*, etc.

**HOMATROPINE** ( $C_{16}H_{21}O_3N$ ) — A white, crystalline, hygroscopic alkaloid, obtained by heating together tropine and mandelic acid; slightly soluble in water, soluble in alcohol and chloroform; m.p. 98° C. It possesses a mydriatic action similar to that of atropine but less powerful and is used in ophthalmology to dilate the pupil of the eye. For this purpose it is usually used as the hydrobromide, a white crystalline salt melting at 214° C. and dissolving in water and alcohol.

**HOMOCYCLIC (Isocyclic)** — A class of organic compounds the molecules of which contain rings of atoms, all of which are identical, *i.e.*, carbon. For example, benzene and all of its derivatives are homocyclic compounds, as also are the cycloparaffins and the cyclic terpenes.

**HOMOGENIZERS** — See Colloid Mill.

**HOMOLOGUES** — Substances having a relative or corresponding position in a series of analogous bodies. For example, the paraffins, the olefines, and the alcohols are three homologous series rising in degrees of the constituent or radical group  $CH_2$ . Substances belonging to such series exhibit, more or less, gradations of many properties. (See Alcohols, and Hydrocarbons.)

**HONEY** contains from 61 to 75 per cent. of glucose (grape sugar, dextrose), less than 1 per cent. sucrose, and is largely used in making foods and preserves. Honey exhibits diastatic power, and the suggestion has been made that the diastase comes from the flowers visited by the bees. The composition of prickly-pear honey of Queensland has been given as follows: water, 20 per cent.; cane sugar, 0·95 per cent.; invert sugar, 77·70 per cent.; dextrin, 0·23 per cent.; mineral matter, 0·11 per cent.; acidity (as formic acid), 0·14 per cent.; and undetermined matter, 0·87 per cent. The unpleasant taste and burning sensation of Noors honey from some south-eastern parts of South Africa, derived from various species of *Euphorbia*, are attributed to some 0·1 per cent. content of a yellow oil. Clarified honey is prepared by the process known as despumation, which consists in allowing molten honey to stand at about 80° C., when the scum rises to the surface and is skimmed off.

**HONEY-STONE or MELLITE** ( $C_{12}Al_2O_{12}, 18H_2O$ ) — A soft resin-like mineral consisting of crystallized native aluminum mellitate occurring in lignite found in Thuringia, Bohemia, and Moravia.

**HONGAY OIL** — From seeds of *Pongamia glabra*; brown and of characteristic odour. Sp. gr. at 15° C., 0·9273 to 0·9385; sap. v., 185·7; i.v. (Winkler), 85·6 to 88·9; contains a number of glycerides, including those of oleic acid 61·30, linolic, 9·72, and palmitic 6·06 per cent., etc.

**HONG KONG OIL** — See Tung Oil.

**HOOF MEAL** is a dried ground mixture of hoof and horn.

**HOPS (*Lupulus*)** — The dried strobiles of *Humulus lupulus* (Fam. Cannabinaceæ) which is cultivated in South-East England, Europe, U.S.A. Pacific Coast, and U.S.S.R. Hops contain a resinous substance which, on storage, becomes oxidized with the production of valerianic acid, and from 0.3 to 1.0 per cent. of volatile oil (see below). The bitter principles present are said to form about 8 to 12 per cent. of the powdered herb and include a sesquiterpene, humulene, and two crystallizable substances named humulone ( $C_{21}H_{30}O_6$ ), and lupulone ( $C_{26}H_{38}O_4$ ).

Hops are cultivated for use in the brewing industry, and it has been estimated that in 1947, the Hops Marketing Board had 155,355 pockets of hops, compared with the figure of 160,820 in 1945 (see J. Nott, *J. Inst. Brew.*, **53**, 141 (1947)). Spent hops constitute a cellulose waste product, produced to the extent of some 12,500 tons annually in Great Britain, and used mainly as hop manure.

Attack by fungal diseases constitutes a serious problem in the cultivation of hops, and a long-term investigation of the genetics of hops has been commenced in the U.S.A. with a view to the production of improved varieties resistant to diseases such as Downy Mildew (see R. E. Fore and J. D. Sather, *J. Inst. Brew.*, **53**, 210 (1947)). A general review of the *Verticillium* wilt problem is given by W. G. Keyworth (*Brew. Trade Rev.*, **61**, 100 (1947)). The fungicidal property of alkaline polysulphides against the conidial phase of hop powdery mildew has been investigated. (See F. H. Beard, *J. Inst. Brew.*, **53**, 212 (1947)).

**HOPS (OIL OF)** — From hop cones, which yield it upon distillation with steam to the extent of from 0.3 to 1.0 per cent., being derived from the lupulin or yellow bitter powder content; green in colour, with the odour of thyme, and said to contain myrcene, geraniol, linalool, humulene, isononoate, luparone, and luparenol. It is soluble in alcohol and ether, has a sp. gr. 0.840 to 0.890 at 15° C. and ref. ind. 1.470 to 1.495 at 20° C. The flowers also yield from 0.3 to about 1.0 per cent. oil.

**HOREHOUND** — The dried leaves and tops of *Marrubium vulgare* (Fam. Labiatæ). Used in confectionery.

**HORMONES** — Organic substances secreted directly into the blood stream which regulate physiological processes in animals. They have been defined as "chemical messengers," a term which well describes their function.

Animal hormones are secreted in special organs, the majority of which discharge their products into the blood stream (ductless glands, or endocrine organs). Some of the important endocrine glands are as follows: pituitary, thyroid, parathyroid, adrenal, pancreas, and certain structures comprising parts of the ovaries and testes. The pituitary gland, situated at the base of the brain, secretes the *trophic hormones*, which appear to regulate the chemical reactions of the body, and in particular the activity of the other endocrine organs. The thyroid secretes *thyroxine*, an iodine-containing amino-acid, which serves to regulate the metabolic rate: lack of thyroxine may cause goitre or

myxœdema, while an excess of thyroxine may cause nervous agitation, and hypersensitivity. The medulla of the adrenal glands secretes adrenaline (epinephrine), which acts to increase blood pressure, as well as other profound physiological effects. The adrenal cortex secretes a mixture of steroid hormones, which regulate the metabolism of salt in the body. Insulin, secreted by the pancreas, converts glucose into glycogen—in which form it is stored in the liver—and insulin deficiency leads to diabetes. Certain cells in the ovaries and testes produce sex hormones, the *estrogens* (female) and *androgens* (male). Many other hormones are produced in the animal body, but their functions are less well understood.

The phytohormones (auxins) are discussed under Plant Hormones. (See *Essentials of Endocrinology*, by A. Grollman (Blakiston, Philadelphia); *Recent Advances in Endocrinology*, by A. T. Cameron (Blakiston, Philadelphia); *The Thyroid Gland*, by C. R. Harrington (Oxford University Press); *The Hormones in Human Reproduction*, by G. W. Corner (Princeton University Press); the use of hormones in animal husbandry, by F. H. Mampress, in *Chem. et Ind.*, 7, 99 (1949); also Adrenalin, Androgens, Corpus Luteum, Enzymes, Estrogens, Insulin, Oestrone, Progesterone, Testosterone, Thyroxin, and Vitamins.)

**HORNBLLENDE (Uralite, Amphibole)**—A mineral consisting of compound silicates of various metals (magnesium, iron, and calcium) in association (crystal system No. 5, and sp. gr. 3 to 3.3). (See Asbestos.)

**HORN MERCURY (Horn Quicksilver)**—See Mercury Compounds.

**HORN SILVER (Cerargyrite, Chlorargyrite)**—Native silver chloride found in some American States (crystal system No. 1, and sp. gr. 5.5).

**HORSEMINT OIL**—See Monarda Oils.

**HORSE-POWER**—The unit of power, being equal to 33,000 foot-pounds of work per minute. 1.34 horse-power=1 kilowatt, and 1 horse-power=1.014 metric horse-power.

**HÜBL NUMBER**—See Fats (Iodine Number).

**HUBNERITE**—Mineral manganese tungstate ( $\text{MnWO}_4$ ) found in certain American States (crystal system No. 5, and sp. gr. 7.17).

**HUME-ROTHERY RULES**—These govern structurally analogous phases in alloy systems and depend on the ratio of valence electron to atoms. The  $\beta$  phases occur at electron-atom ratios of 3 : 2,  $\gamma$  phases at 21 : 13, and  $\epsilon$  phases at 7 : 4. (See Physics of Metals.)

**HUMIDITY**—See Air, Dew-Point, Hygograph, Hygrometer, and Water.

**HUMUS**—Decayed vegetable matter, probably formed from lignin in soil, by the various activities of insect life, fungi, and bacteria. It contains a substance called humic acid, which decomposes into carbon dioxide and water at 80° C. Oxidation of phenols in alkaline solution leads to the formation of substances which exhibit the properties of natural humic acids, one of them having the formula  $\text{C}_6\text{H}_4\text{O}_3$ . They can also be prepared from furfural. Humus is supposed under one

view to be formed by the oxidation of quinones, which arise in their turn from hexoses by the elimination of water. Another view is that carbohydrates decompose to form a body named hydroxymethylfurfuraldehyde, which then condenses to form humus. The soluble part of humus contains about 50 to 57 per cent. carbon, 35 per cent. oxygen, 3 to 8 per cent. nitrogen, and is constantly undergoing decomposition by action of air, moisture, bacteria, moulds, and enzymes.

**HYDROCARPUS OIL** — A fatty oil obtained by cold expression from *Hydnocarpus Wightiana*, the seeds of which yield about 41 per cent. of the oil. It contains the glycerides of chaulmoogric and hydnocarpic acids, sp. gr. 0.950 to 0.960 at 25° C., m.p. 20° to 25° C., and sap. v. 198 to 204. The ethyl esters of the fatty acids of hydnocarpus oil are used in medicine for the treatment of leprosy. The oil obtained from *H. Illicifolia*, which grows extensively in Siam, is stated to be very similar. (See Chaulmoogra Oil.)

**HYDRARGILLITE**  $\text{Al}(\text{OH})_3$  — Crystal system No. 3, and sp. gr. 2.3.

**HYDRASTINE**  $(\text{C}_{21}\text{H}_{21}\text{O}_6\text{N})$  — A white, poisonous alkaloid of m.p. 133° C. from the root of *Hydrastis canadensis* ("golden seal"), growing in Canada and eastern part of the U.S.A., which, as also the hydrochloride  $(\text{C}_{21}\text{H}_{21}\text{O}_6\text{N}, \text{HCl})$ , was formerly used in medicine. It is chemically allied to narcotine, and possesses a similar physiological action, causing a rise in blood pressure by constriction of the small vessels and depressing the heart. On oxidation it yields hydrastinine  $(\text{C}_{11}\text{H}_{12}\text{O}_2\text{N})$ , a white crystalline substance of m.p. 117° C. (See *The Plant Alkaloids*, by Henry (Churchill, London); and, for the synthesis of hydrastrine, Hope *et al.* (*J. Chem. Soc.*, 1931, 236).)

**HYDRATES** — This term is now reserved for compounds containing  $\text{H}_2\text{O}$ , as, for example,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ . (See Acids.)

**HYDRAZINE (Diamide)**  $(\text{N}_2\text{H}_4 \text{ or } \text{NH}_2\text{.NH}_2)$  — A colourless liquid of sp. gr. 1.011, b.p. 113.5° C., made by reduction from nitrosamine, and manufactured by interaction of sodium hypochlorite and ammonia in the presence of glue. Hydrazine is a base, slightly weaker than ammonium hydroxide, and forms two series of salts, such as monohydrochloride and dihydrochloride. It is a powerful reducing agent, reducing cupric salts to cuprous, silver salts to silver, and mercury salts to mercury. Its thermal decomposition under varying conditions was studied by P. J. Askey, who found, amongst other results, that it decomposes on quartz at 270° to 310° C. as follows:  $3\text{N}_2\text{H}_4 = 4\text{NH}_3 + \text{N}_2$ . (See *The Chemistry of Hydrazine*, by L. F. Audrieth and Betty A. Ogg (John Wiley and Sons, New York); Nitrosamines, and Phenylhydrazine.)

**HYDRAZOIC ACID (Hydrogen Azide, Azoimide)**  $(\text{HN}_3)$  — A colourless, white, mobile liquid of explosive character, which can be prepared from hydrazine hydrate; also from sodamide and nitrous oxide by acidification of the sodium hydrazoate thus produced  $(\text{NH}_2\text{Na} + \text{N}_2\text{O} = \text{NaN}_3 + \text{H}_2\text{O})$ , and distillation. The pure acid boils at 37° C., and is monobasic; it attacks many metals, such as zinc and aluminium, hydrogen

and ammonia being evolved. Its vapour is decomposed by ultraviolet radiation from an aluminium spark ; hydrogen, nitrogen, and ammonia in the form of ammonium azide being formed (Beckman and Dickinson). Its salts are known both as hydrazoates and as azides. (See Azides.)

**HYDRAZONES** — Products of reaction between carbonyl ( $>CO$ ) compounds and hydrazine acetate. The hydrazones have the formula  $R.CH:N.NH_2$ , R being an alkyl or aryl radical (usually aryl), and result from condensation of aldehydes (or ketones) with hydrazine. The melting points are characteristic of the various aldehydes and ketones, and frequent use is made of this fact in the identification of these compounds. Melting point of acetophenone phenylhydrazone  $105^\circ C.$ ; benzaldehyde phenylhydrazone  $155^\circ C.$ ; benzophenone phenylhydrazone  $137^\circ C.$ ; cinnamaldehyde phenylhydrazone  $168^\circ C.$ ; cyclohexanone phenylhydrazone  $77^\circ C.$ ; furfural phenylhydrazone,  $97^\circ C.$ ; and salicylaldehyde phenylhydrazone  $142^\circ C.$  (See Phenylhydrazine)

**HYDRIDES** — A term given to combinations of hydrogen with other elements: (1) Solids of high melting point, potassium hydride (KH), sodium hydride (NaH), lithium hydride (LiH), calcium hydride ( $CaH_2$ ), strontium hydride ( $SrH_2$ ), and barium hydride ( $BaH_2$ ); and (2) volatile compounds, boron hydride (borobutane ( $B_4H_{10}$ ), b.p.  $10^\circ C.$ ); hydrocarbons, silicon hydride ( $SiH_4$ ), germanium hydride ( $GeH_4$ ); ammonia ( $NH_3$ ), phosphine ( $PH_3$ ), arsine ( $AsH_3$ ), stibine ( $SbH_3$ ); water, hydrogen sulphide ( $H_2S$ ), hydrogen selenide ( $H_2Se$ ), hydrogen telluride ( $H_2Te$ ); hydrogen fluoride ( $H_2F_2$ ), hydrogen chloride (HCl), hydrogen bromide (HBr), and hydrogen iodide (HI). More than one hydride is known in the case of boron, carbon, silicon, nitrogen, phosphorus, arsenic, and oxygen, as chief instances.

Calcium hydride can be produced by the action of hydrogen gas on molten metallic calcium or on calcium chloride at  $550^\circ C.$  and upwards, when hydrochloric acid gas is evolved, and electrolysis of the hydrides of the group to which calcium hydride belongs shows the liberation of calcium at the cathode and hydrogen gas at the anode (signifying negative hydrogen in these hydrides). Lithium hydride and calcium hydride are important sources of portable hydrogen, since hydrogen gas is evolved simply upon treatment with water.

**HYDRIODIC ACID** — See Iodine Compounds.

**HYDRION (Hydrogen-Ion)** — The positively charged hydrogen atom. (See Hydrogen-Ion Determination, and Volumetric Analyses.)

**HYDROBROMIC ACID** — See Bromine Compounds.

**HYDROCARBONS** — Combinations of carbon and hydrogen, constituting a large body of organic compounds of great interest and importance. The more important ones may be roughly classified as follows:

(1) The **Paraffins** — A series of homologous, saturated, aliphatic hydrocarbons of the general formula  $C_nH_{2n+2}$ , incapable of combining further with hydrogen or halogens and comparatively indifferent to chemical action. The lower and best-known members are shown with their formulas, boiling-points, and specific gravities.

## PARAFFIN HYDROCARBONS. THEIR BOILING-POINTS AND SPECIFIC GRAVITIES

Name	Formula	Boiling-point ° C.	Specific Gravity at 20° C.
Methane .. ..	CH <sub>4</sub>	-161.5	—
Ethane .. ..	C <sub>2</sub> H <sub>6</sub>	-88.6	—
Propane .. ..	C <sub>3</sub> H <sub>8</sub>	-42.1	—
<i>n</i> -Butane .. ..	C <sub>4</sub> H <sub>10</sub>	-0.6	—
2-Methylpropane (isobutane) .. ..	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>3</sub>	-11.7	—
<i>n</i> -Pentane .. ..	C <sub>5</sub> H <sub>12</sub>	+36.1	0.626
2-Methylbutane (isopentane) .. ..	(CH <sub>3</sub> ) <sub>2</sub> CHC <sub>2</sub> H <sub>5</sub>	+27.9	0.620
2,2-Dimethylpropane (neopentane) .. ..	(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	9.5	—
<i>n</i> -Hexane .. ..	C <sub>6</sub> H <sub>14</sub>	68.7	0.659
<i>n</i> -Heptane .. ..	C <sub>7</sub> H <sub>16</sub>	98.4	0.684
<i>n</i> -Octane .. ..	C <sub>8</sub> H <sub>18</sub>	125.7	0.703
<i>n</i> -Nonane .. ..	C <sub>9</sub> H <sub>20</sub>	150.8	0.718

These hydrocarbons exhibit a step-by-step rise of CH<sub>2</sub> and a gradual rise in the specific gravities. Methane, ethane, and propane are known to have each one isomeric form, while butane has two, pentane at least three, and hexane five known ones, while most of the higher paraffins are known in various forms.

**Methane** is a colourless, odourless gas known as a constituent of "marsh gas" and "fire-damp," and often results from the decomposition of organic matter under water in marshes and stagnant pools. It burns with a faintly luminous flame, forms an explosive mixture with air or oxygen, its ignition in admixture with air being to some extent dependent upon the nature of the igniting source. As generated from decaying vegetable matters and by the intensive fermentation process of sewage treatment (due to the bacterial fermentation of cellulose) it has been utilized as a motive power in connection with gas plant.

Supplies of the natural gas of approximately 97.19 per cent. purity are now produced in a Welsh mine, and there is a natural gas from Tariki, Taranaki, consisting of almost pure methane. Natural gas is abundant in Texas, California, Oklahoma, Louisiana, the combined production of these four states representing 80 per cent. of the total natural gas production of 3.9 millions of millions (3.9 × 10<sup>12</sup>) cubic feet in 1945 in the United States.

Coal gas contains from 35 to 40 per cent. methane.

Methane can be liquefied at -164° C. and solidified at -186° C. It is produced when a mixture of carbon monoxide and hydrogen is passed over nickel at 220° to 280° C. (2CO + 2H<sub>2</sub> = CO<sub>2</sub> + CH<sub>4</sub> and CO + 3H<sub>2</sub> = CH<sub>4</sub> + H<sub>2</sub>O); also when a mixture of carbon dioxide and hydrogen is passed over nickel deposited on magnesia at

328° C. ( $\text{CO}_2 + 4\text{H}_2 = \text{CH}_4 + 2\text{H}_2\text{O}$ ) ; or nickel carbide ( $\text{Ni}_3\text{C}$ ) can alternatively be used as the catalyst. Ruthenium oxide is a good catalyst, and quantitative results, it is stated, can be obtained at 250° C. by the use of cobalt oxide to which 15 per cent. alumina has been added. It is stated that methane can be almost completely converted into acetylene in the arc-oven, while acetylene admits of polymerization to a tarry body about half of which consists of benzene.

The explosion wave for methane and oxygen has a velocity of 2,322 metres per second.

Incomplete combustion of methane yields carbon black ; high temperature pyrolysis yields carbon black plus hydrogen or acetylene gas, an important source of these substances ; steam with a catalyst yields carbon monoxide plus hydrogen, a source for Fischer-Tropsch synthesis of liquid hydrocarbons ; air with a catalyst yields methanol, thence formaldehyde ; and chlorine yields methyl chloride, methylene chloride, chloroform, and carbon tetrachloride, the last being a source for fluorochloromethanes as coolants. (See Formaldehyde, Marsh Gas, Nitrogen, Sewage, and Water Gas.)

**Ethane** is a gas contained in crude petroleum, and can be prepared by the electrolysis of sodium acetate, by the reduction of ethyl haloids, and otherwise. Like methane, it burns with a slightly luminous flame. It decomposes at 550° C., the chief products being methane and ethylene.

**Propane and Butane** are also gases, while the next three members of the series are colourless, mobile, inflammable liquids found in paraffin oil as obtained from cannel coal and in petroleum. These hydrocarbons are now prepared from the "wet gas" of natural petroleum wells in the U.S.A. on a large scale, and are variously employed as fuel, for lighting, and for solvent extraction of petroleum lubricating oils. See "Liquid Propane," by R. E. Wilson *et al.* (*Ind. Eng. Chem.*, **28**, 1065 (1936)), for use in dewaxing, deasphalting, and refining petroleum oils ; and M. H. Tuttle in *Proceedings of the American Petroleum Institute*, **16**, Pt. III, 112 (1935).

**Pentane** — The ordinary or normal pentane ( $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$ ) is a colourless, mobile, inflammable, pleasant-smelling liquid of sp. gr. 0.626, b.p. 36.1° C., and m.p. -131.5° C., soluble in alcohol and ether, obtained by fractional distillation from petroleum. It is used in the 10-candle pentane Harcourt lamp, sometimes also as an anæsthetic, and in the manufacture of ice. It is also used in the manufacture of amyl chloride, amyl alcohol, and amyl acetate ; the chloride being made by interaction of its hot vapour with chlorine gas, and the chloride in its turn is employed in the manufacture of amyl alcohol. (See Amyl Alcohol.) There are two other isomers of pentane.

**Hexane and Heptane** are colourless inflammable liquids obtained from petroleum by fractional distillation, and used as solvents. Various **octanes** are discussed under Petroleum (Cracking).

The liquid paraffins are all soluble in alcohol and ether, but not in water. (See Petroleum.)

The homologues from pentane up to those containing 17 carbon atoms

inclusive are liquid at 20° C., while the higher members are colourless and solid.

(2) The **Olefin** or **Ethylene** series is a class of unsaturated (acyclic) hydrocarbons of ascending boiling-points and general formula  $C_nH_{2n}$  (containing one ethylenic double bond), and named after the corresponding paraffin hydrocarbons by adding "ylene" to the stem or, at the present time, by changing the suffix "ane" to "ene."

The first three members of the group are colourless gases, and both ethylene and propylene in admixture with oxygen have proved of value as anæsthetics. Methylene (methene,  $CH_2$ ) is not known to exist. When the liquid members are reached (with amylene) they diminish in mobility, while the higher ones, like cerotene ( $C_{27}H_{54}$ ) and melene ( $C_{30}H_{60}$ ), are solid. These last-named substances can be obtained from china wax and beeswax respectively by distillation. Amylene (trimethylethylene)  $((CH_3)_2C:CH.CH_3)$ , obtained by heating ordinary amyl alcohol with zinc chloride, is a mobile inflammable liquid of b.p. 35° C., sp. gr. 0.666, and disagreeable odour, sometimes used as a local anæsthetic. Several amylene dichlorides are used as solvents.

The olefins readily combine with nascent hydrogen, chlorine, etc., readily polymerize, and are easily attacked by potassium permanganate and chromic anhydride ( $CrO_3$ ). Most of them are soluble in alcohol and ether, but not in water. The best-known member of the series is ethylene (known also as ethene and olefiant gas), a colourless gas, slightly soluble in water and alcohol and known as a constituent of coal and coke-oven gases, from which it can be obtained. It is prepared by the passage of carbon monoxide and hydrogen gases over a catalyst such as finely divided nickel or platinum at 100° C.; by the decomposition of ethyl alcohol vapour in the presence of a heated catalyst, such as aluminum oxide; also by action of sulphuric acid or syrupy phosphoric acid upon its corresponding alcohol ( $CH_3.CH_2OH = CH_2:CH_2 + H_2O$ ). It burns with a luminous flame and is valuable for the preparation of nitroglycerol, also as a constituent of non-freezing nitro-explosives, for the preparation of mustard gas, the synthesis of ethyl alcohol, for preserving fruit, and for turning the green tints of oranges and grape fruit to a yellow or golden colour, for which purpose minute amounts of the very dilute gas suffice.

By combination with chlorine, ethylene forms ethylene dichloride ( $C_2H_4Cl_2$ ), and at low temperatures it reacts with ozone to form an explosive ozonide, which upon treatment with water is hydrolysed as follows:  $C_2H_4O_3 + H_2O = 2HCHO + H_2O_2$ . (See Ethylene for Chart of Its Industries.)

Propylene is available in the gases from petroleum refining, and is made into (1) isopropyl alcohol by reaction with sulphuric acid followed by hydrolysis, thence into (a) methyl methacrylate and its resins, and (b) acetic anhydride for cellulose acetate plastics, and (2) allyl chloride by reaction with chlorine, thence into glycerol.

Butylenes in three isomeric forms are known:  $\alpha$  of b.p. -5° C.,  $\beta$  of b.p. +10° C., and  $\gamma$  of b.p. -6° C.; and there are five isomeric amylenes.

## OLEFIN HYDROCARBONS. THEIR BOILING-POINTS AND SPECIFIC GRAVITIES

Common Name	Name	Formula	Boiling Point ° C.	Specific Gravity at 20° C.
Ethylene	Ethene	$C_2H_4$	-104	—
Propylene	Propene	$CH_3.CH : CH_2$	-48	—
Butylene	1-Butene	$C_4H_8.CH : CH_2$	-6	—
	<i>cis</i> -2-Butene	$\begin{Bmatrix} CH_3.CH \\ CH_3.\ddot{C}H \\ CH_3.CH \end{Bmatrix}$	+4	—
	<i>trans</i> -2-Butene	$\begin{Bmatrix} CH_3.CH \\ HC.\ddot{C}H_3 \end{Bmatrix}$	+1	—
	2-Methylpropene (isobutene)	$(CH_3)_2C : CH_2$	-7	—
Amylene	1-Pentene	$C_5H_{10}.CH : CH_2$	+40	—
Hexylene	1-Hexene	$C_6H_{12}.CH : CH_2$	64	0.68
Heptylene	1-Heptene	$C_7H_{14}.CH : CH_2$	99	0.70
Octylene	1-Octene	$C_8H_{16}.CH : CH_2$	123	0.72

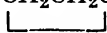
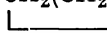
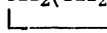
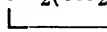
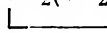
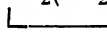
The **Diolefin** series of general formula  $C_nH_{2n-2}$  contain two ethylenic double bonds in each member.

## DIOLEFIN HYDROCARBONS. THEIR BOILING POINTS AND SPECIFIC GRAVITIES

Name	Formula	Boiling Point °C.	Specific Gravity at 20° C.
Propadiene (allene) ..	$CH_2 : C : CH_2$	-34.5	—
1,2-Butadiene. . .	$CH_3CH : C : CH_2$	+10.3	0.65
1,3-Butadiene. . .	$CH_2 : CH.CH : CH_2$	-4.4	0.62
1,2-Pentadiene ..	$CH_3CH_2CH : C : CH_2$	+45	0.69
<i>cis</i> -1,3-Pentadiene ..	$\begin{Bmatrix} CH_3CH \\ CH_2 : CH\ddot{C}H \\ CH_3CH \end{Bmatrix}$	44	0.69
<i>trans</i> -1,3-Pentadiene	$\begin{Bmatrix} CH_3CH \\ \ddot{C}HCH : CH_2 \end{Bmatrix}$	42	0.68
1,4-Pentadiene ..	$CH_2 : CHCH_2CH : CH_2$	26	0.66
2,3-Pentadiene ..	$CH_3CH : C : CHCH_3$	40	0.66
3-Methyl-1,2-butadiene	$(CH_3)_2C : C : CH_2$	40	0.68
2-Methyl-1,3-butadiene (isoprene)	$\begin{Bmatrix} CH_2 : CH.C : CH_2 \\   \\ CH_3 \end{Bmatrix}$	34	0.68
1,2-Hexadiene ..	$CH_3(CH_2)_2CH : C : CH_2$	78	0.72

(3) The **Cycloparaffin (Naphthene)** series consists of saturated ring hydrocarbons of general formula  $C_nH_{2n}$ , isomeric with monoölefins, and correctly called cycloalkanes, less frequently polymethylenes. (See Cyclohexane, and Cyclopropane.)

CYCLOPARAFFIN HYDROCARBONS. THEIR BOILING POINTS AND  
SPECIFIC GRAVITIES

Name	Formula	Boiling Point °C.	Specific Gravity at 20° C.
Cyclopropane .. ..	$CH_2CH_2CH_2$ 	-34	—
Cyclobutane .. ..	$CH_2(CH_2)_2CH_2$ 	+13	—
Cyclopentane .. ..	$CH_2(CH_2)_3CH_2$ 	49.3	0.741
Methylcyclopentane ..	$CH_2(CH_2)_3CHCH_3$ 	71.8	0.744
Cyclohexane .. ..	$CH_2(CH_2)_4CH_2$ 	81	0.779
Methylcyclohexane ..	$CH_2(CH_2)_4CHCH_3$ 	101	0.769

(4) The **Acetylene** aliphatic series of general formula  $C_nH_{2n-2}$ , including acetylene ( $C_2H_2$ ), contain the trivalent methenyl radical: CH or  $H.C\equiv$  and 2 atoms of hydrogen less than the olefins; they are gaseous up to  $C_4H_6$ , the intervening ones are liquid, and the highest members are solid. (See Acetylene for Chart of Its Industries.)

(5) The **Benzene Hydrocarbons**, of which the best-known members are Benzene, Toluene, and Xylene (see same).

See *Physical Constants of Mononuclear Aromatic Hydrocarbons*, by Gustav Egloff and A. V. Grosse (Universal Oil Products Booklet No. 217 (1938)), for data on more than 180 compounds.

(6) The **Benzenoid Hydrocarbons**. Several groups having benzene nuclei, including naphthalene ( $C_{10}H_8$ ), anthracene ( $C_{14}H_{10}$ ), diphenyl ( $C_6H_5.C_6H_5$ ) (see same).

(7) The **Terpenes** ( $C_{10}H_{16}$ ) — A series of unsaturated isomeric hydrocarbons of the formula  $C_{10}H_{16}$ , having boiling-points ranging from 155° to 185° C., all of which are liquid with the exception of camphene. As they exist in essential oils, they are mixtures of terpenes and not chemical individuals, and are often associated with oxidized bodies allied to and, in many cases, derived from them.

Pinene (dextro-pinene) is the chief terpene contained (80 to 85 per cent.) in the American and German turpentine oils; b.p. about 156° C., *sn. gr.* 0.8587 at 20° C. and *ref. ind.* 1.465 at 20° C.

BENZENE HYDROCARBONS. THEIR BOILING-POINTS AND  
SPECIFIC GRAVITIES

Name	Formula	Boiling Point °C	Specific Gravity at 20°C
Benzene .. ..	$C_6H_6$	80.1	0.878
Toluene .. ..	$C_6H_5.CH_3$	110.6	0.866
<i>o</i> -Xylene .. ..	$C_6H_4(CH_3)_2(1,2)$	144.4	0.879
<i>m</i> -Xylene .. ..	$C_6H_4(CH_3)_2(1,3)$	139.1	0.865
<i>p</i> -Xylene .. ..	$C_6H_4(CH_3)_2(1,4)$	138.3	—
Ethylbenzene .. ..	$C_6H_5.C_2H_5$	136.2	0.868
<i>n</i> -Propylbenzene .. ..	$C_6H_5(CH_2)_2CH_3$	159.2	0.862
Isopropylbenzene (cumene)	$C_6H_5.CH(CH_3)_2$	152.4	0.864
<i>o</i> -Methylethylbenzene ..	$C_6H_4(CH_3)(1)$ $(C_2H_5)(2)$	165.2	0.881
<i>m</i> -Methylethylbenzene ..	$C_6H_4(CH_3)(1)$ $(C_2H_5)(3)$	161.3	0.865
<i>p</i> -Methylethylbenzene ..	$C_6H_4(CH_3)(1)$ $(C_2H_5)(4)$	162.0	0.861
1,2,3-Trimethylbenzene (hemimellitene)	$C_6H_3(CH_3)_3(1,2,3)$	176.1	0.894
1,2,4-Trimethylbenzene (pseudocumene)	$C_6H_3(CH_3)_3(1,2,4)$	169.3	0.876
1,3,5-Trimethylbenzene (mesitylene)	$C_6H_3(CH_3)_3(1,3,5)$	164.7	0.865
1-Methyl-4-isopropyl- benzene ( <i>p</i> -cymene)	$C_6H_4(CH_3)(1)$ $CH(CH_3)_2(4)$	177.1	0.857

Lævo-pinene is the chief constituent of French turpentine, whilst carene, sylvestrene, and hemi-terpene (dipentene) ( $C_5H_8$ ), together with pinene, are contained in varying proportions in the Russian and Swedish oils.

Indian turpentine contains pinene and two terpenes named *carene* and *longifolene*. Oil of orange contains limonene. Fennel oil and some eucalyptus oils contain phellandrene.

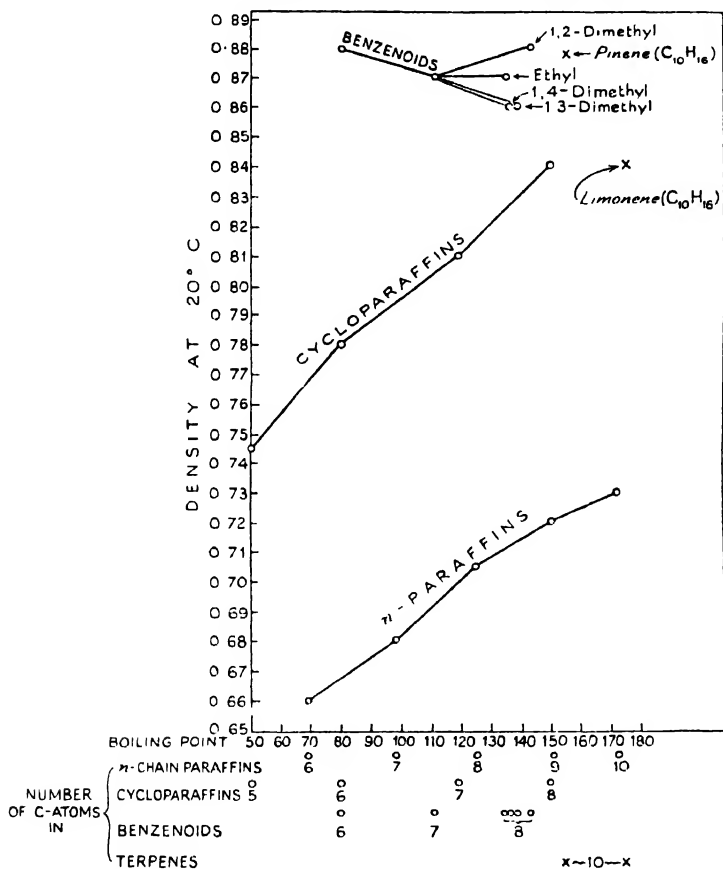
Citrene is contained in the oil of citron, hesperidene in the oil of orange, thymene in the oil of thyme, carvene in the oil of cumin, phellandrene in eucalyptus oil and the oil of *Melaleuca acuminata*, etc.

The terpenes form additive compounds, such as the dihydrochlorides,  $C_{10}H_{18}Cl_2$ ; tetrabromides,  $C_{10}H_{16}Br_4$ ; nitrosochlorides,  $C_{10}H_{16}(NOCl)_2$ , etc., most of which are well-defined crystalline compounds with definite melting-points.

The associated hydrocarbons of the formula  $C_5H_8$ , known as hemi-terpenes, include isoprene; those of the formula  $C_{15}H_{24}$  are termed

"sesquiterpenes," including cadinene, caryophyllene, cedrene, santalene; and diterpenes ( $C_{20}H_{32}$ ), such as carene, among other polyterpenes. (See also Dipentene, Essential Oils, and Isoprene.) Isoprene is the best-known hemi-terpene ( $C_5H_8$ ), whilst dipentene ( $C_{10}H_{16}$ ) is associated with cineol in *Oleum cinæ*, and can be easily prepared from

### HYDROCARBONS: NORMAL PARAFFINS, CYCLOPARAFFINS, MONOBENZENOIDS, AND TWO TERPENES



GRAPH SHOWING DENSITIES AT 20° C., AND BOILING POINTS

pinene and some other terpenes. These compounds are further referred to in the descriptions of the various essential oils in which they occur or under their distinct names.

(See J. A. Nieuwland's Nichols Medal address on "Synthesis from Unsaturated Hydrocarbons" in *Ind. Eng. Chem.*, **27**, 850 (1935); *Non-Benzenoid Hydrocarbons*, by B. T. Brooks (Reinhold Publishing Corp.,

New York) ; *Selected Values of Properties of Hydrocarbons*, Circular 461 (1947), National Bureau of Standards, Washington, D.C. ; *Physical Constants of the Principal Hydrocarbons*, by M. P. Doss (The Texas Company, New York) ; *Data Book on Hydrocarbons*, by J. B. Maxwell (D. Van Nostrand Co., New York) ; *Physical Chemistry of Hydrocarbons*, by A. Farkas (Academic Press, New York).)

**HYDROCHLORIC ACID** — See Chlorine.

**HYDROCYANIC ACID (HYDROGEN CYANIDE or PRUSSIC ACID)**

(HCN) is a colourless, volatile gas of b.p.  $26^{\circ}\text{C}$ ., solidifying at  $-14^{\circ}\text{C}$ ., sp. gr. 0.70, and of peculiar odour like that of bitter almonds. It is the active agent of the killing bottle used by entomologists, an effective vermifuge, and has been used in India for the disinfection of railway carriages and in the U.S.A. for the disinfection of ships. It is being increasingly used as a fumigant for the destruction of insects and vermin pests in or on foods, and its effects on foods therefore call for special attention. It is exceedingly poisonous, and as it is without taste, a person eating it has little warning until collapse occurs.

Hydrogen cyanide is formed by the passage of electric sparks through a mixture of acetylene and nitrogen, and can also be obtained by distillation from the kernels of bitter almonds or prepared by the action of dilute sulphuric acid upon potassium cyanide (from which mixture the acid can be distilled over with water). As used for fumigating purposes, it is generated by allowing 50 per cent. solutions of sodium cyanide and sulphuric acid to flow and mix together upon a platform within the generator, using a stream of air to convey the gas to the place of application. Another process is based upon the action of moisture on dry calcium cyanide, the hydrocyanic acid being generated, it is alleged, rapidly and evenly. The calcium cyanide thus employed is described as "powdered hydrocyanic acid," and contains an average of 55 per cent. cyanogen. (See Calcium Cyanide, and Cyanamide.)

In a pure state it may be obtained by passing hydrogen sulphide over dry mercuric cyanide:  $\text{Hg}(\text{CN})_2 + \text{H}_2\text{S} = 2(\text{HCN}) + \text{HgS}$ . It is also produced by action of the silent electric discharge on a mixture of cyanogen and hydrogen, and one of the commercial processes of production is conducted by the passage of a dried mixture of hydrogen, ammonia, and either carbon monoxide, carbon dioxide, or acetylene over heated platinized pumice.

Solutions of calcium cyanide, when boiled, yield all the cyanogen as hydrocyanic acid, and moist carbon dioxide at a pressure lower than atmospheric is stated to effect a quantitative liberation of the acid from sodium or calcium cyanide without loss from polymerization. It is also manufactured from cyanamide and sodium chloride with single-phase electric current and subsequent treatment with sulphuric acid.

In closed containers, explosions are apt to occur owing to the generation of gas caused by exothermic polymerization and decomposition of the liquid. Upon keeping in contact with water, it undergoes change into ammonium formate:  $\text{HCN} + 2\text{H}_2\text{O} = \text{H.COONH}_4$ . It is soluble in water, alcohol, and ether, and by combination with

bases forms cyanides; a large number of double cyanides are also known. "Hydro-Cy" (Du Pont) is the trade mark for a 96 per cent. strength of hydrocyanic acid, used in the fumigation of citrus fruit trees.

The leaves of Sudan grass yield, it is stated, hydrocyanic acid upon digestion of the macerated material by the action of enzymes; it is also a constituent of the juice of the tapioca plant, and cherry-laurel leaves contain about 0.253 per cent.

**HYDRO-EXTRACTORS** — See Centrifuges.

**HYDROFERRICYANIC ACID** — See Cyanogen Compounds.

**HYDROFERROCYANIC ACID** — See Cyanogen Compounds.

**HYDROFLUORIC ACID** — See Fluorine Compounds.

**HYDROFLUOSILICIC ACID** — See Silicon Compounds, and Lead.

**HYDROFORMING** — The conversion of low-octane-number naphthas into stable high-octane gasoline. The principal conversions are, namely, (1) six-membered rings of cycloparaffins into the corresponding aromatics by loss of hydrogen; (2) five-membered rings of cycloparaffins (*a*) into aromatics by loss of hydrogen, and (*b*) into lower boiling-point paraffins by cracking; (3) paraffins (*a*) into aromatics by loss of hydrogen and ring formation, and (*b*) into lower boiling-point paraffins by cracking. The temperature used is 480° to 540° C., the pressure 150–300 pounds per square inch including a high partial pressure of hydrogen to diminish carbon formation, and a catalyst of molybdena on alumina (1941, industrially).

**HYDROGEN (H) and its Compounds** — Atomic weight, 1.0080. See Elements for other data. Hydrogen does not exist to any considerable extent in nature in the free gaseous state, although it is believed to be present in very large amount in the atmosphere of the sun. At ordinary temperatures it is a colourless gas, soluble to some extent in water (1 volume of which at 0° C. dissolves 0.021 volume of the gas), is without taste or smell, and is the lightest known substance, so that the relative weights of all other elements were formerly compared with hydrogen as the unit.

M. Poljakov reports that when hydrogen is circulated over a palladium plate previously heated to 700° to 800° C. and cooled at 1 to 5 mm. to 300° to 400° C. a violet luminescence is observed. It can be activated by bubbling through molten sodium, or by the action of heat and water on sodium hydride, or by adsorption on the platinum metals.

There are two forms of gas differing in boiling and freezing points which K. Bonhoeffer describes as ortho-hydrogen and para-hydrogen. See *Orthohydrogen, Parahydrogen, and Heavy Hydrogen*, by A. Farkas (Macmillan Co., London and New York).

**Heavy Hydrogen (Deuterium) (D)** is the isotope of mass 2 of ordinary hydrogen, and constitutes 2 parts of 10,000 of the latter. It is obtained by prolonged electrolysis of water, the ordinary lighter isotope of mass K.C.E.—18

1 being changed to hydrogen gas more rapidly leaves a higher concentration of deuterium in the electrolytic cell. Deuterium was discovered by H. C. Urey in 1932. Deuterium monoxide ( $D_2O$ ) is the chemical name for "heavy water," and it is interesting to compare its properties with those of ordinary water: Melting-point of  $D_2O$   $+3.8^\circ$  C. (of  $H_2O$   $0.0^\circ$  C.); boiling-point  $101.4^\circ$  C. (of  $H_2O$   $100.0^\circ$  C.); temperature of maximum density  $+11.6^\circ$  C. (of  $H_2O$   $4.0^\circ$  C.); density at  $25^\circ$  C. 1.1056 (of  $H_2O$  1.0000); and solubility of sodium chloride 15 per cent. less than in ordinary water.

"Heavy hydrogen" furnishes deuterons of twice the mass of protons for atomic bombardment (see Nuclear Chemistry, and Radioactivity (Artificial)). Experiments performed with "heavy hydrogen" in the field of organic chemistry enable the experimenter to "tag the atoms" of hydrogen and thus to follow their course in reactions. Great significance attaches to this in the field of biochemistry, and the tracing of tagged hydrogen in the animal organism. (See Willard Gibbs Medal Address by H. C. Urey on "The Significance of the Hydrogen Isotopes" (*Ind. Eng. Chem.*, 26, 803 (1934)).)

**Tritium** — See same.

Metals, certain oxides, and other substances, when introduced into a stream of **atomic hydrogen**, are raised to incandescence owing, it is said, to the surface of the substance acting as a catalyst in bringing about the re-combination of the atoms; while hydrogen produced by blowing a current of hydrogen from a narrow tube into the electric arc is capable of melting molybdenum and tungsten with ease.

In its ordinary form, hydrogen is a comparatively inactive substance, but in its active form it is capable of reducing potassium permanganate to the lower manganate, indigo blue to indigo white, and combining with nitrogen to form ammonia. This activated hydrogen is, however, very unstable, and is stated to revert to the inactive state in less than one minute. Under pressure it acquires active properties, and in contact with some materials, such as the dust of iron oxide, hydrogen will ignite.

Hydrogen gas is inflammable, and when a stream of it is burned in the air or oxygen gas it forms water by combination ( $2H_2 + O_2 = 2H_2O$ ). A mixture of hydrogen and oxygen gas (or air) in certain proportions will explode when a light or electric spark is applied to the mixture, water being thus produced in the same way as when a stream of hydrogen is burned in the air. It has been shown, however, that mixtures of hydrogen and oxygen, which have been desiccated by prolonged exposure to phosphorus pentoxide, can be heated to redness in Jena glass tubes without explosion occurring, although slow combination ensues upon heating in presence of the least degree of moisture. H. B. Baker and Miss M. Carlton have shown that when the gases have been dried for seven or eight weeks, there is no appreciable contraction after some hours' exposure to ultra-violet light produced by a quartz mercury lamp, and therefore no formation of water.

In the **liquid** state, hydrogen is as clear and colourless as water, having boiling point  $-253^\circ$  C.

The gas is easily made in the laboratory by the action of dilute sulphuric acid upon the metal zinc ( $\text{Zn} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2$ )—that is to say, the metal is attacked and dissolved by the acid, forming zinc sulphate, which passes into solution, the hydrogen escaping in the form of gas. It is also obtainable from coke-oven gas, which contains approximately 50 per cent. hydrogen.

Hydrogen, prepared by industrial processes, is often used in the oxy-hydrogen flame for welding; also to fill the bags or floating chambers of airships; in a number of industries, including the production of methyl alcohol, liquid fuels, and ammonia; and in the hydrogenation of oils for use in the manufacture of soap and margarine, the oils being converted by this process into solid fats by the assimilation or absorption of hydrogen, for example, oleic acid ( $\text{C}_{17}\text{H}_{33}\text{COOH}$ ) absorbs 2 atoms hydrogen, and becomes converted into stearic acid ( $\text{C}_{17}\text{H}_{35}\text{COOH}$ ). For catalytic hydrogenation processes the hydrogen used must be very pure. A new use for hydrogen by the General Electric Co., Schenectady, is that for cooling enclosed moving electrical machinery, which will thus handle 50 per cent. more power without increasing the safety limit in point of temperature.

The hydrogen for these and other purposes may be prepared by several processes, one of which is conducted by passing steam over coke at a high temperature, 6 tons of coke yielding about 1 ton of hydrogen; another is carried out by passing the vapour of water at a high temperature over iron prepared in a spongy condition, by which the oxygen combines with the iron and the hydrogen gas is set free. One of the best-known plants for effecting this process is the "Lane-Rogers," as installed by the Fuel Research Board, and it has been found that iron oxide deposited on pumice stone reacts more effectually than the spathic iron ore when used in the same plant. In the "Bosch" process a mixture of steam and water gas is passed over a catalyst at about  $400^\circ$  to  $500^\circ \text{C}$ . Another process producing very pure hydrogen is conducted by the electrolysis of an aqueous solution of caustic soda in a series of cells, hydrogen being evolved at the cathode and oxygen at the anode, and collected separately.

A "cracking" process, conducted by the passage of ammonia gas over a catalyst at  $600^\circ \text{C}$ ., furnishes hydrogen (75 per cent., along with 25 per cent. of nitrogen) for the cutting of metals, the reduction of metallic oxides, and other manufacturing operations.

Electrolytically prepared hydrogen can only be used for many purposes where electric energy is both cheap and abundantly available, approximately 140 kw.h. per 1,000 cubic ft. gas being necessary, while the oxygen simultaneously produced is relatively difficult of disposal.

The "Silicol" process consists in the decomposition of silicon alloys, such as ferro- or mangano-silicons (obtained in the electric furnace), by a strong solution of caustic soda containing from 35 to 40 per cent. of NaOH, the heat generated by dissolving the caustic in water being sufficient to start the reaction,  $\text{Si} + 2\text{NaOH} + \text{H}_2\text{O} = \text{Na}_2\text{SiO}_3 + 2\text{H}_2$ . Hydrogen can also be made by the action of water on an alloy of magnesium and lead; and by the reaction of water with either lithium

or calcium hydride, a convenient method for producing hydrogen upon demand.

Another important method depends upon the catalytic oxidation of the carbon monoxide of water gas by superheated steam, and then separating the carbon dioxide thus formed from the remaining hydrogen by pressure through water. There are also several biochemical processes by which hydrogen can be made, one of which is referred to under the heading of Acetone. Hydrogen for "synthesis gas," containing also carbon monoxide, is referred to under Fuels (Liquid).

There are two compounds of hydrogen and oxygen—viz. water ( $\text{H}_2\text{O}$ ) and hydrogen peroxide (dioxide) ( $\text{H}_2\text{O}_2$ ). With the halogens, it forms the acids known as hydrochloric ( $\text{HCl}$ ), hydrobromic ( $\text{HBr}$ ), hydriodic ( $\text{HI}$ ), and hydrofluoric ( $\text{H}_2\text{F}_2$ ).

Combinations of hydrogen with nitrogen and oxygen are known in the forms of nitrous acid ( $\text{HNO}_2$ ), and nitric acid ( $\text{HNO}_3$ ); and with sulphur and oxygen in the forms of sulphurous and sulphuric acids ( $\text{H}_2\text{SO}_3$  and  $\text{H}_2\text{SO}_4$ ). Hydrogen is a constituent of innumerable organic compounds, including the hydrocarbons, and with carbon and nitrogen it forms hydrocyanic acid ( $\text{HCN}$ ). With sulphur alone it forms the compounds hydrogen sulphide ( $\text{H}_2\text{S}$ ) and hydrogen persulphide ( $\text{H}_2\text{S}_2$ ), an oily liquid of sp. gr. 1.376 and unstable character. With nitrogen alone it exists in combination as ammonia ( $\text{NH}_3$ ), and hydrazine ( $\text{N}_2\text{H}_4$ ) and, along with oxygen, hydroxylamine ( $\text{H}_2\text{NOH}$ ); and it forms so-called hydrides with many metals, such as arsenic and antimony, and sodium and calcium (see Hydrides).

**Hydrogen Bomb (H-Bomb)** — See Fusion Reaction.

**Hydrogenation** is a process available for the production of petrol and oil from coal or the crude products of coal carbonization. As applied to fatty oils it is brought about by the influence of so-called *catalytic agents*, the metal nickel (from 0.25 to 1 per cent. of the weight of the oil) being most economically used for this purpose in association with silicates (such as the kieselguhr which comes from Stavanger, Norway) or other materials. Generally, nickel carbonate or hydroxide is deposited on the carrier, and subsequently reduced to metallic nickel at about  $350^\circ\text{C}$ ., but sometimes gaseous nickel carbonyl is used. The purity of the nickel is of importance, the catalytic poisons to be suspected in association with nickel salts being lead, zinc, and sulphur. (See Nickel.) Palladium, platinum, cobalt, and other metals can also be used as catalysts.

The catalytic agent has, of course, to be brought into contact with the cleaned oils to be treated, and the mixture heated to from  $160^\circ$  to  $200^\circ\text{C}$ . in purified hydrogen at a pressure of about 10 atmospheres, and there are many modifications of plant for effecting this. Many oils, such as whale oil, otherwise difficult to purify and having objectionable properties, are thus deodorized and turned into solid fats more easily and economically adapted for soap-making, or made more or less fit for edible use, while it is also possible to increase the melting-points of vegetable oils, thus rendering them available for making margarine.

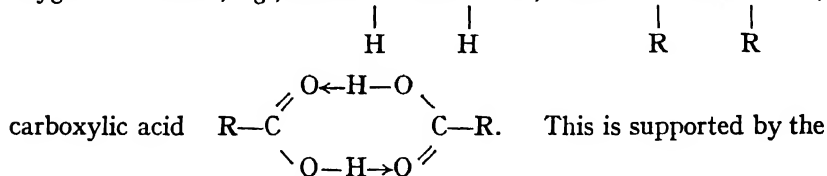
There is a so-called hydrogenation odour and flavour attached to these

commercial products obtained from fish and vegetable oils, originating, as suggested, in the formation of some volatile aldehydic and ketonic bodies, and only when this difficulty is overcome can the hydrogenated oils be used in compounding delicate edible products. The best method, so far known, of deodorizing hardened fats is by exposure under ordinary pressure to a mixture of carbon dioxide and nitrogen for a period of from 40 to 50 minutes.

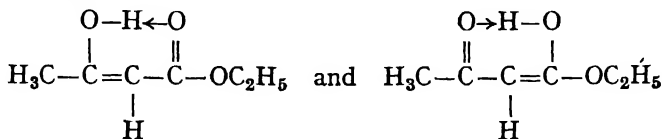
Fat-hardening is applied to the oils obtained from sesame seed, cottonseed, and ground nuts (earth nuts, peanuts). After refining, they are mixed with the catalyst (very finely divided nickel oxide or salt) and heated to from 100° to 260° C. in a high steam-jacketed autoclave, the hydrogen being introduced through pipes into the mixture.

Hydrogenation is a process of importance in the production of synthetic ammonia; in the preparation of cyclohexane from benzene; cyclohexanol from phenol; of "Tetralin" and allied products from naphthalene; the possible production of aniline by a catalytic process from nitrobenzene; and the hydrogenation of coal. The hydrogenated phenols like "Hexalin" have many industrial applications by reason of their powerful solvent and emulsifying properties. (See "Dekalin," "Hexalin," Hydrogenated Phenols; *Hydrogenation of Organic Substances*, by C. Ellis (Routledge and Sons, London); Discussion of "Hydrogenation of Coal" in *Ind. Eng. Chem.*, **36**, 291-298 (1944); Berginization, Coal, and Nitrogen Fixation.)

**HYDROGEN BONDING (Chelation)** — The formation of a coordinate linkage between the hydroxyl hydrogen of one molecule and the oxygen of another, e.g., water  $\text{O}-\text{H} \leftarrow \text{O}-\text{H}$ ; alcohol  $\text{O}-\text{H} \leftarrow \text{O}-\text{H}$ ;

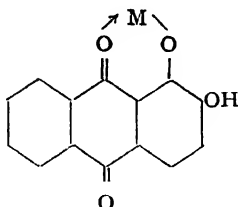


observation that the boiling points of these compounds are higher than would be anticipated, therefore association is assumed. Acetoacetic ester is believed to be of similar structure but of two resonating enol forms, namely:



The equilibrium mixture of keto-enol tautomers contain in the vapour phase 45 per cent. enol. The common type of chelate ring is that in acetoacetic ester consisting of six atoms and two double bonds. This type may also be that present in alizarin (and other) lakes with metals

(M) such as aluminium ( $\text{Al}^{+++}$ ), chromium ( $\text{Cr}^{+++}$ ) or iron ( $\text{Fe}^{+++}$ ).  
 thus :



**HYDROGEN CHLORIDE** — See Chlorine.

**HYDROGEN CYANIDE** — See Hydrocyanic Acid.

**HYDROGEN DIOXIDE** — See Hydrogen Peroxide.

**HYDROGEN-ION** — All acids have some common properties such as sour taste, ability to change the colour of indicators, reaction with active metals to give hydrogen, and with metallic oxides and hydroxides to form salts and water. All these properties are due to the presence of the hydrogen-ion which is common to all aqueous-acid solutions. There is considerable evidence, both direct and indirect, indicating that the hydrogen-ion is not the free proton but that it is combined with one or more molecules of solvent, *i.e.*, water. This evidence includes X-ray analysis of crystalline perchloric acid hydrate ( $\text{HClO}_4 \cdot \text{H}_2\text{O}$ ); the conductivity of water and hydrogen bromide in liquid sulphur dioxide as compared to the non-conductivity of water and sulphur dioxide, and of hydrogen bromide and sulphur dioxide; and the studies of Dole (*J. Amer. Chem. Soc.*, **54**, 3095 (1932)) with the glass electrode demonstrating that "as the hydrogen-ion migrates through the glass (membrane) it carries exactly one molecule of water along with it."

Hydrogen-ion concentration can be expressed in a number of ways (see Concentration) but is usually expressed in moles per litre or *pH* units. A *pH* unit is expressed as the negative logarithm of the hydrogen-ion concentration expressed in moles per litre, *i.e.*,  $\text{pH} = -\log (\text{H}^+)$ .

Determination of the hydrogen-ion concentration or *pH* is generally done by means of indicators, or electrometrically by the *pH* meter. Certain organic compounds (indicators), generally weak acids or bases, show colour changes when the hydrogen-ion concentration is changed. The particular range on the *pH* scale where a given indicator changes colour is a characteristic property of the individual indicator. A series of indicators is known that will by colour changes cover the entire range from a highly acid to a highly basic solution. The following list of indicators and their *pH* range covers the range of *pH* from 0 to 14. (For example, Methyl Orange 2.9–4 means that this indicator undergoes a colour change between the range of 2.9 to 4 *pH* units.) Methyl Red (para) 0–2; Methyl Violet 0–2; Thymol Blue 1.2–2.8 and 8.0–9.6; Ethyl Orange 2–4; Congo Red 3–5; Methyl Orange 2.9–4;

Bromcresol Green 3·8–5·4; Methyl Red 4·4–6; Propyl Red 4·8–6·4; Bromphenol Red 5·2–6·8; Bromthymol Blue 6·7–6; Neutral Red 6·8–8; Phenol Red 6·8–8·4; Cresol Red 7·2–8·8; Phenolphthaleïn 9·3–10·5; Alizarin Yellow G 10·1–12·1; Alizarin Blue S 11–13; Sodium Indigodisulphonate 12–14.

The *pH* meter is an electrometric method of determining the hydrogen-ion concentration utilizing, generally, the glass electrode for the hydrogen-ion against a standard half-cell, usually the calomel cell. The voltmeter is generally calibrated directly into *pH* units.

*References:* *The Determination of Hydrogen Ions*, by W. Mansfield Clark (Williams and Wilkins Company, Baltimore); *Hydrogen Ions, Their Determination and Importance in Pure and Industrial Chemistry*, by H. T. S. Britton (D. van Nostrand Company, New York); *pH and Electro-Titrations*, by I. M. Kolthoff and H. A. Laitinen (John Wiley and Sons, New York and London); *Hydrogen-Ion Concentration and Its Practical Applications*, by F. L. LaMotte *et al.* (Williams and Wilkins, Baltimore); *Measurement of Hydrogen-Ion Concentration*, by J. Grant (Longmans, Green and Co., London); and *pH Value*.

**HYDROGEN PEROXIDE** or **HYDROGEN DIOXIDE** ( $\text{H}_2\text{O}_2$ ) is nearly related to water, and differs therefrom in that its molecule contains 1 atom more oxygen. It can be prepared in a number of ways, one of which consists in mixing barium peroxide ( $\text{BaO}_2$ ) with dilute sulphuric acid, when the following interaction takes place:  $\text{BaO}_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + \text{H}_2\text{O}_2$ . It can also be prepared from sodium peroxide and water. Another method consists in treating barium peroxide in the presence of water with carbon dioxide under pressure. The dilute solution of hydrogen peroxide resulting from these processes, after separation from the insoluble barium sulphate or carbonate, can be concentrated to some extent by evaporation, or it can be purified by distilling at a low pressure and concentrated up to 90 per cent. by an appliance known as the "sulphuric acid concentrator," and from this solution 100 per cent. peroxide can be obtained by fractional freezing. A further process for making it is by electrolysing sulphuric acid (using a platinum anode), and the subsequent conversion of the persulphuric acid thus produced into hydrogen peroxide. It is stated that sodium persulphate can be produced to a greater degree of concentration than the free acid, and that distillation of the once recrystallized sodium salt gives reasonably high yields of the peroxide. By electrolysis  $2\text{KHSO}_4$  gives  $\text{K}_2\text{S}_2\text{O}_8$  and  $\text{H}_2$ ; by distillation,  $\text{K}_2\text{S}_2\text{O}_8$  and  $2\text{H}_2\text{O}$  gives  $2\text{KHSO}_4$  and  $\text{H}_2\text{O}_2$ . It is produced in appreciable quantity when air or oxygen is rapidly passed through water containing palladium foil thoroughly saturated with hydrogen. The urea compound named "Hyperol" yields hydrogen peroxide by hydrolysis with water. Hydrogen peroxide is always found amongst the products which result when ether, phosphorus, turpentine, and terpenes generally are exposed to air and moisture, so that it is always present in the air of pine woods and eucalyptus forests, also following lightning discharges, and under some other circumstances. Ether that has been

## SPECIFIC GRAVITIES (DENSITIES) ON TWADDELL'S HYDROMETER.

Compared with water at 15.56° C. or 60° F.

Degrees	Sp. Gr.	Degrees	Sp. Gr.	Degrees	Sp. Gr.	Degrees	Sp. Gr.
0	1.000	15	1.075	25	1.125	35	1.175
5	1.025	20	1.100	30	1.150	40	1.200
10	1.050						

stem floats above the surface of the liquid, the density of which is to be determined. Sike's hydrometer for ascertaining the alcoholic strength of spirituous liquors is constructed on this principle, and there are tables made out so that the graduations on the stem correspond to definite percentages of alcohol, water being marked as zero of the standard.

It is important in determining densities by means of hydrometers to pay great attention to the temperature, as small differences in that respect make considerable variations in the result. It is usual to observe at a temperature of 15.56° C., or 60° F., at which temperature the hydrometer is graduated.

The degrees of Twaddell's hydrometer are convertible into corresponding specific gravities by multiplying them by 0.005 and adding 1.000.

The number of degrees Balling scale (° B.) (per cent. by weight of sugar in solution) is obtained from the formula :

$$\text{Specific Gravity at } 17.5^{\circ} \text{ C.} = \frac{200}{200 \pm \text{Degrees Balling'}}$$

$$\text{Or, Degrees Balling} = 1 \pm \frac{200}{\text{Specific Gravity at } 17.5^{\circ} \text{ C.}}$$

(See also A.P.I. Scale, Densities, and Specific Gravities.)

**HYDRONE** — See Water.

**HYDROQUINONE or QUINOL (1, 4-Dihydroxybenzene)** ( $\text{C}_6\text{H}_4(\text{OH})_2$ ) — A white, crystalline, dihydroxy phenol, used in medicine, and as a developer in photography on account of its strong reducing action. It can be obtained by the reduction of quinone with sulphur dioxide, or from natural sources by hydrolysis of the glucoside arbutin, occurring in the leaves of bearberry. It is soluble in water, alcohol, and ether, and melts at 170° C. (See Glycosides, and Tanning.)

**“HYDROS”** — A trade name for sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), used as a decolorizing agent, by removal of iron compounds from soap after the process of saponification is completed (2 to 3 lb. being used for every 1,000 lb. of fats); also for decolorizing sugar solutions during the refining process, and in calico-printing for discharging the colour in certain portions of the pattern. (See Hydrosulphites.)

**HYDROSOLS** — See Colloid Chemistry.

**HYDROSULPHIDES (Sulphydrates)** contain the group—HS. If potassium be heated in gaseous hydrogen sulphide, potassium hydrosulphide

is formed, hydrogen being at the same time set free:  $\text{H}_2\text{S} + \text{K} = \text{KHS} + \frac{1}{2}\text{H}_2$ ; and the same substance is produced in solution by passing a current of hydrogen sulphide into a solution of potassium hydroxide, carbonate, or sulphide until no further change takes place.

Sodium hydrosulphide ( $\text{NaHS}, 2\text{H}_2\text{O}$ ) can be obtained in the form of colourless needles, soluble in water, by treating calcium sulphide with sodium bisulphate. (See Mercaptans.)

**HYDROSULPHITES** — Sodium hydrogen sulphite ( $\text{NaHSO}_3$ ) and sulphur dioxide plus zinc dust yields sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) plus zinc sulphite ( $\text{ZnSO}_3$ ). Removal of zinc by calcium hydroxide, and saturating the filtrate with sodium chloride yields crystals of sodium hydrosulphite. Sodium hydrosulphite can also be obtained by the electrolytic (cathodic) reduction of sodium hydrogen sulphate:  $2 \text{NaHSO}_4 + 2\text{H} = \text{Na}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O}$ . This salt is a strong reducing agent, and is used to bleach indigo blue, and sugar solutions.

Hydrosulphites are marketed in three forms, namely, sodium hyposulphite, in white lumps or small white crystals readily soluble in water, having an odour of sulphur dioxide, and which acts without the addition of acid; another form, namely, a sodium compound—known as "Formosul," usually employed in solution with formic or acetic acid; and zinc "Formosul," which contains zinc instead of sodium. This last is the most stable and powerful of the three, and is said to be the best to use for stripping colours.

**HYDROXAMIC ACIDS** — See Nitroparaffins.

**HYDROXIDES** — Compounds containing the radical  $-\text{OH}$  combined with a metallic ion or radical. The common soluble hydroxides are the bases sodium hydroxide ( $\text{NaOH}$ ), potassium hydroxide ( $\text{KOH}$ ), ammonium hydroxide ( $\text{NH}_4\text{OH}$ ), Barium hydroxide ( $\text{Ba}(\text{OH})_2$ ), strontium hydroxide ( $\text{Sr}(\text{OH})_2$ ), and calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) are moderately soluble, and the remaining common hydroxides are relatively insoluble. Insoluble hydroxides are readily prepared by precipitation of a salt solution of the metal in question with a soluble hydroxide solution, followed by separation of the resulting precipitate, usually by filtration. (See Acids and Bases.)

#### DISSOCIATION PRESSURES AND TEMPERATURES OF SOME HYDROXIDES

Hydroxide	Dissociation Pressure mm. Hg.	Corresponding Temperature ° C.
$\text{Ca}(\text{OH})_2$ ..	760	540
$\text{Sr}(\text{OH})_2$ ..	760	880
$\text{Ba}(\text{OH})_2$ ..	760	995
$\text{Mg}(\text{OH})_2$ ..	760	160
$\text{Zn}(\text{OH})_2$ ..	760	125
$\text{Pb}(\text{OH})_2$ ..	760	150
$\text{Al}(\text{OH})_3$ ..	760	320

**HYDROXY ACETIC ACID** (Du Pont) ( $\text{CH}_2\text{OH}.\text{COOH}$ ) — A liquid of 70 per cent. strength, used in tanning, in dyeing of textiles and leather, and in adhesives and cleaning mixtures.

**HYDROXYL** (OH) — The monad (univalent) radical group which exists in many chemical combinations, such as the hydroxides, *e.g.*, sodium hydroxide ( $\text{NaOH}$ ), the alcohols, *e.g.*, ethyl alcohol ( $\text{CH}_3.\text{CH}_2\text{OH}$ ), and the phenols, *e.g.*, phenol ( $\text{C}_6\text{H}_5\text{OH}$ ).

**HYDROXYLAMINE** ( $\text{NH}_2\text{OH}$ ) — A colourless, crystalline, basic derivate of ammonia, of m.p.  $34^\circ\text{C}$ ., used as a reducing agent, etc. It may be regarded as ammonia in which a hydrogen atom is replaced by the hydroxyl group (OH). It is prepared by the action of nascent hydrogen upon nitric oxide or nitric acid, the hydrogen being generated from tin and hydrochloric acid, and in their presence hydroxylamine hydrochloride is formed. From this salt, when separated, hydroxylamine is generated by decomposition with a base and distillation *in vacuo*. It forms salts with acids by addition, *e.g.*, hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}.\text{HCl}$ ), and with bases, *e.g.*, sodium hydroxylamite ( $\text{NH}_2\text{ONa}$ ); and oximes (see same) with aldehydes and ketones.

Hydroxylamine decomposes with explosive violence if heated to about  $100^\circ\text{C}$ . It is a powerful reducing agent in solution, changing cupric ion to cuprous oxide in alkaline solution; silver ion to silver; and mercury ion to mercury. The hydrochloride is used as a photographic developer.

**HYGIENE (Chemistry of)** — See *Theory and Practice of Hygiene*, by Notter and Firth (J. and A. Churchill, London); *A Textbook of Hygiene*, by J. R. Currie (E. and S. Livingstone, Edinburgh); and *Hygiene*, by R. C. Whitman (Chapman and Hall, London).

**HYGROGRAPH** — The so-called clock-driven baro-thermo-hygrograph (Negretti and Zambra) records on one chart with three distinct traces the barometric pressure, temperature, and humidity. "Casella's hair hydrograph" is an instrument for recording on a chart percentages of humidity based on the property of human hair, when free from fat, of expanding in moist air and contracting in dry air. A bundle of hair is held by two jaws, and at the centre supports a hook attached to a system of levers; the tension of the bundle of hairs actuates the recording pen through a pair of cams working on each other. (See Humidity, and Hygrometers.)

**HYGROMETERS** — Special varieties of these instruments are made for determining the humidity of the air in timber, leather, and paper-drying rooms; there is also a "whirling" make recommended by the "Hot and Deep Mines" Temperature Committee. The hair hygrometer acts by the contraction or expansion of a strand of specially treated hair, which alters in length according to the percentage of moisture in the air, the movement being conveyed to an indicator. (See Water.)

**HYGROSCOPIC** — The property of absorbing moisture from the air, as in the case of concentrated sulphuric acid, glycerol, calcium chloride, and many other substances. When these are exposed to air, ordinarily the substance absorbs or condenses water vapour from the air. This can only occur when the water vapour pressure of the air is greater than the water vapour pressure of the solution in question at the same temperature.

**HYOSCINE HYDROBROMIDE (Scopolamine Hydrobromide)** ( $C_{17}H_{21}O_4N$ ,  $HBr \cdot 3H_2O$ ) — A colourless, crystalline alkaloidal salt, being the hydrobromide of *l*-hyosine (*l*-scopolamine) obtained from various plants of the family Solanaceæ, notably species of *Datura* and *Scopola*; soluble in water and alcohol; m.p.  $194^\circ$  to  $196^\circ$  C. It has a pharmacological action similar to that of atropine but produces more depression of the motor areas of the brain; it is used in medicine for the production of "twilight sleep" in labour and as a remedy for sea-sickness; it is also administered prior to surgical operations. (See Atropine, Belladonna, Hyoscyamus, and Stramonium.)

**HYOSCYAMINE** ( $C_{17}H_{23}O_3N$ ) — A colourless crystalline alkaloid obtained from various solanaceous plants, notably *Hyoscyamus muticus* (Egyptian Henbane); sparingly soluble in water; soluble in alcohol, ether, and chloroform; m.p.  $106^\circ$  to  $108^\circ$  C. It has a pharmacological action intermediate between that of atropine and hyosine and is used in medicine as an antispasmodic and hypnotic. (See Atropine, Belladonna, Hyoscyamus, and Stramonium.)

**HYOSCYAMUS** — The dried leaves and flowering tops of *Hyoscyamus niger*, a solanaceous plant found in England and Europe. It contains from 0.05 to 0.1 per cent. of alkaloids, the chief constituent being hyoscyamine together with small amounts of atropine and hyosine. The drug is used in medicine in the form of a tincture as an antispasmodic. (See Atropine, Belladonna, and Hyoscyamine.)

**"HYPEROL"** — The registered name of a white crystalline compound of hydrogen dioxide and urea ( $CO(NH_2)_2 \cdot H_2O_2$ ), which yields 35 per cent.  $H_2O_2$  by hydrolysis with water. One gram dissolved in 10 c.c. water yields a 10-volume solution of peroxide in association with the urea.

**HYPO** — A prefix in chemical nomenclature used to distinguish a particular compound from other members of a series, as, for example, nitrous and nitric acid, the term hyponitrous acid indicating the acid containing the least oxygen.  $HNO_2$  is nitrous acid,  $HNO_3$  is nitric acid, and  $H_2N_2O_2$  is hyponitrous acid. Hypochlorous acid is  $HOCl$ , hyposulphurous acid or hydrosulphurous acid is  $H_2S_2O_4$  (distinction from  $H_2S_2O_3$ , which is thiosulphuric acid), and hypophosphorous acid is  $H_3PO_2$  (a monobasic acid,  $H \cdot H_2PO_2$ ).

**"HYPO"** — This trade term is also used as a common name for sodium thiosulphate.

**HYPOCHLORITES** — Salts of hypochlorous acid. (See Chlorine (Compounds).)

**HYPOCHLOROUS ACID** — See Chlorine (Compounds).

**HYPOPHOSPHOROUS ACID** — See Phosphorus (Compounds).

**HYPOSULPHITE OF SODIUM** — See Sodium (Compounds).

**HYPOSULPHITES** — See Hydrosulphites.

**HYSSOP OIL** — A colourless essential oil distilled from the herb *Hyssopus officinalis* (N.O. Labiatae), the yield being 0.4 per cent. ; soluble in alcohol and ether, of sp. gr. 0.932, and used in perfumery, medicine, and liqueur-making.

*i* — An abbreviation for optically inactive. The use of the single letter is to be deprecated and it is customary to designate inactive racemic (externally compensated) mixtures by the prefix DL or *dl*. Internally compensated forms are referred to as *meso*. (See Stereoisomerism.)

**"IALINE"** — A disinfectant of coal-tar nature miscible with water.

**ICE** — See Water, and Heat.

**ICE (DRY)** — See Carbon Oxides (Carbon Dioxide).

**ICELAND MOSS** — A dried lichen, *Cetraria islandica*, which is indigenous to Great Britain and grows abundantly on the coasts of Norway, Iceland, and other parts of the Northern Hemisphere. Iceland Moss consists of carbohydrates which are converted to dextrose on boiling with dilute mineral acid. The carbohydrate constituents are stated to consist of lichenin which is soluble in hot water, forming a gel on cooling, and *isolichenin* which is soluble in cold water and may possibly be a mixture. Iceland moss also contains a bitter principle, fumaro-protocetraric acid, which on hydrolysis yields fumaric and cetraric acids. (See Fumaric Acid.)

**ICELAND SPAR** — See Calcium (Carbonate).

**ICHTHAMMOL** ("Ichthyl," Ammonium Ichthosulphonate) — An indefinite mixture of ammonium salts of the sulphonic acids prepared by treating the oil distilled from bituminous schists with sulphuric acid. The schists are composed of the remains of fish and marine animals and, on distillation, yield from 1 to 10 per cent. of a black oil which contains about 10 per cent. of organically combined sulphur. Ichthammol is used in medicine as a mild antiseptic for the treatment of certain skin conditions such as acne and eczema. The oil from Kashpir shale differs from that produced from the Scottish shale.

**"ICHTHYOL"** — See Ichthammol.

**"ICYL"** — A group of colours presenting certain advantages with respect to dyeing viscose silk substitutes. (See Dyes, and Silk Substitutes.)

“IGEPO” — See Soaps (Sulphated Alcohol).

**IGNITION** — Setting on fire or taking light. A piece of paper ignites on applying a lighted match. A jet of coal gas takes light in the same way, and both the paper and the gas are thus ignited and burn with production of light and heat. The temperature at which combustion of a substance takes place is known as its ignition-point. It is not always necessary to apply a light to cause combustion; phosphorus takes fire on exposure to the air, and if sodium be simply warmed in the air it also will burn, forming the peroxide ( $\text{Na}_2\text{O}_2$ ). Again, lime in slaking may develop sufficient heat to set fire to wood in close proximity.

The “ignition temperature” of gases may be roughly described as the lowest at which a mixture of combustible gas and air or oxygen will undergo chemical change, thus producing flame. The “lag” in ignition, usually defined as the interval in time between the rapid heating of the mixture to or above a certain minimum temperature called the ignition point and the appearance of flame is a function of several conditions. (See Flame, and Flash-Point.)

**ILANG-ILANG OIL** — See Ylang-ylang.

**ILLICIUM OIL** — See Aniseed Oil.

**ILLIPÉ TALLOW** — An edible fat from the illipé nuts of Borneo, Indo-China, Sumatra, and neighbouring islands, obtained from various dipterocarp trees, including *Shorea stenoptera* (Burck), distinct, however, from the Indian nuts yielded by species of *Bassia* (Sapotaceæ), which give the softer fat known as illipé butter. The component glycerides of Borneo (Illipé) tallow were the subject of an investigation by Hilditch and Priestman, the specimen in question exhibiting a m.p. of  $36^\circ$  to  $36.5^\circ$  C., sap. v. 290.7, i.v. 32.3, while the mixed fatty acids comprised stearic acid 39 per cent., oleic acid 38 per cent., palmitic acid 21.5 per cent., and myristic acid 1.5 per cent.

There is much confusion concerning the product known variously as illipé “tallow,” “butter,” and “nut oil,” all derived from various families of so-called butter-trees. For instance, kernels from the Kinabatangan district, containing 6.9 per cent. moisture, are stated to yield (by extraction with petroleum) 44.8 per cent. fat, which has the general character of Borneo tallow, with an acid value of 11.4 as compared with previous samples, reported at from 45 to 73. The residual meal contains 10.3 per cent. protein, and constitutes a cattle foodstuff. Again, Singapore nuts are stated to yield 50 to 55 per cent. oil, sp. gr. 0.9021 at  $40^\circ/4^\circ$  C., m.p.  $39^\circ$  to  $40^\circ$  C., i.v. 50 to 64, and sap. v. 188.4.

**ILMENITE** — A mineral compound of iron and titanium oxides,  $(\text{FeTi})\text{O}_3$ , of crystal system No. 3, and sp. gr. 4.5 to 5.1. The deposit at Egerdund (south of Stavanger) is stated to have the composition  $\text{Fe}(\text{Mg})\text{TiO}_3, 10\text{Fe}_2\text{O}_3$ . Large deposits occur in Canada and the Travancore State, while that found in Johore (Malay Peninsula) contains 46.5 per cent. titanium oxide. (See Titanium.)

**IMIDES** — Anhydrides of certain acids in which the oxygen atom is replaced by the divalent group ( $:NH$ ).

Succinimide ( $C_2H_4(CO)_2NH$ ) is a crystalline substance, of m.p.  $125^\circ C.$ , formed by heating ammonium hydrogen succinate. Orthophthalimide ( $C_6H_4(CO)_2NH$ ) is a white crystalline body, of m.p.  $238^\circ C.$ , used in the production of indigo, and made by dissolving phthalic anhydride in ammonia, evaporation to dryness, and fusion of the residue. (See Amides, and Amines.)

**IMINO (IMIDO) GROUP** — The divalent group ( $:NH$ ). (See Imides.)

**IMPERMEABLE** — Fabrics rendered waterproof by various processes are described as impermeable to water. Stone surfaces can be rendered more or less impermeable, and thus secured to some extent against atmospheric attack, by washing over with sodium silicate or silicon ester, and varnishes give impermeability to the surfaces of various articles.

**INCI-GRASS OIL** — An essential oil distilled from *Cymbopogon flexuosus*, a grass growing wild on the slopes of Travancore; sp. gr. 0.920 to 0.923; sap. v. about 5.6; acet. v. about 120. The commercial oil contains varying proportions of borneol, camphene, limonene, and terpineol, and can be used as a substitute for palmrosa oil, which it resembles in odour.

**INCINERATION** — The process of reduction to ashes by burning or ignition. (See Destructors, and Wastes.)

**INDAMINES** — A group of dyestuffs obtained from the indo-anilines by substitution of the group  $-NH_2$  for the quinone oxygen—for example, "phenylene blue" or indamine ( $NH_2.C_6H_4.N : C_6H_4 : NH$ ), made by oxidizing a mixture of aniline and *p*-phenylenediamine.

**INDANTHRENE (Blue)** — A vat dye, very fast and stable, and of several varieties; usually made by alkaline fusion of 2-aminoanthraquinone.

**INDENE** ( $C_6H_4.CH : CH.CH_2$ ) — A clear, heavy, mobile liquid, of b.p.

$182^\circ C.$ , contained in that fraction of crude benzol which comes over at from  $176^\circ$  to  $182^\circ C.$  It rapidly absorbs oxygen from the air, and by exposure to air and sunlight forms polymerides. When heated to  $190^\circ$  to  $200^\circ C.$ , it is quickly transformed into a resinous mass of polymerized resultants. (See Coumarone, and Gums and Resins (Synthetic).)

**INDIAN GUM** — See Gums and Resins (Bassora).

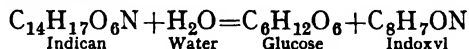
**INDIAN HEMP** — See Cannabis.

**INDIAN INK (Chinese Ink)** — See Inks.

**INDIAN RED** — Some varieties consist of nearly pure ferric oxide ( $Fe_2O_3$ ), but the natural pigment from the Persian Gulf contains ferric silicate ( $Fe_2O_3.SiO_2$ ). Imitations of the natural oxides are prepared by the action of acids on iron and precipitation of hydroxides or carbonates from the solution, followed by calcination.

**INDIA-RUBBER (Caoutchouc)** — See Rubber.

**INDICAN (Indoxylglucoside)** — The active principle of the indigo plant, from which indigo blue is obtained. It can be obtained in a crystalline form in combination with 3 molecules of water, and is of the character of a glycoside, being hydrolysed by dilute acids, or the plant enzymes to glucose and indoxyl :



Indoxyl is readily oxidized by air to indigotin (indigo).

**INDICATORS** — Substances that show the beginning or end of a chemical reaction, for example, litmus in testing for acids and bases, and starch in testing for free iodine. Indicators to show various concentrations of hydrogen-ion are much used. Yamada's universal indicator is patented and reported to consist of 5.0 mg. thymol blue, 12.5 mg. methyl red, 60 mg. bromthymol blue, 100 mg. phenolphthalein dissolved in 100 ml. of 95 per cent. ethyl alcohol, neutralized with 0.05 molar sodium hydroxide to a green colour, and then made up to 200 ml. with water. The various colours at different values of *pH* are : red, 4 ; orange, 5 ; yellow, 6 ; green, 7 ; blue, 8 ; indigo, 9 ; violet, 10. (See Analytical Chemistry, Hydrogen-Ion, *pH* Value, and Volumetric Analyses.)

**INDIGO or INDIGOTIN** — The formula  $\text{C}_{16}\text{H}_{10}\text{O}_2\text{N}_2$  is supported by its vapour density, while the formula  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2$  is given as that of indigo-white. Indigo is a blue colouring matter, being an indigoid vat dyestuff, prepared from the herbaceous shrubs *Isatis tinctoria* (N.O. Leguminosæ), *Polygonum tinctoria*, and other plants, and formed from indican, which exists in the juice. *Indigofera leptostachya*, cultivated in Java and indigenous in Natal, is reported to be superior to *Indigofera tinctoria*, and even better results are credited to *Indigofera erecta*. Well-made samples are said to contain 70 per cent. of the glucoside associated with other substances (known as "indirubin," and "indigo brown"), which have an influence in the dye-vat, and which probably account for the alleged superiority of natural indigo over manufactured indigo made synthetically from naphthalene or phthalic acid.

In the synthetic production of indigo, starting with naphthalene, it is first of all oxidized to phthalic acid, and this by sublimation is converted into phthalic anhydride ( $\text{C}_6\text{H}_4(\text{CO})_2\text{O}$ ), which when heated in presence of ammonia yields phthalimide ( $\text{C}_6\text{H}_4(\text{CO})_2\text{NH}$ ), and this compound, when subjected to the action of alkalis and an alkaline hypochlorite, produces anthranilic acid ( $\text{C}_6\text{H}_4.\text{NH}_2.\text{COOH}$ ). By interaction with monochloroacetic acid, anthranilic acid gives phenylglycine-*ortho*-carboxylic acid, and this when melted with an alkali and made into solution is oxidized by a current of air, thereby producing indigo blue (indigotin).

Another process consists in treating aniline with chloroacetic acid, thus producing the phenylglycine ( $\text{C}_6\text{H}_5.\text{NH}.\text{CH}_2.\text{COOH}$ ), which when heated with sodamide ( $\text{NH}_2\text{Na}$ ), or metallic sodium in the presence

of ammonia, yields indigo blue through oxidation of the intermediate compound (indoxyl)  $(\text{C}_8\text{H}_4\text{C}(\text{OH})\text{:CH.NH})$ . For an account of the

manufacture of indigo as carried out at the Monthey works in Switzerland, see *Ind. Chem.*, 2, 557 (1926). Indigo can also be synthesized from fumaric acid and aniline. A further process (Lepetit's), stated to be used by E. I. du Pont de Nemours and Co., consists in treating aniline with formaldehyde and sodium bisulphite, and then treating the product of that reaction with sodium cyanide, forming phenylglycine nitrile, which is subsequently fused with alkali hydroxide.

Indigo sublimes at  $300^\circ\text{C.}$ , and is insoluble in water, but soluble in aniline, glacial acetic acid, nitrobenzene, and chloroform, and dissolves in hot strong sulphuric acid to a deep blue colour; it is this solution of indigosulphuric acid that is used in dyeing. By oxidation with nitric acid indigo yields isatin.

Natural **Indigo Blue** is prepared by cutting the plants just before flowering and steeping in water for twelve or more hours, when a fermentation takes place, yielding a yellow-coloured liquor, which is then drawn off, and subsequently agitated in contact with the air, in which process oxygen is absorbed and the indigo is thrown down as a greenish-blue precipitate. This is strained off, pressed, dried, and cut up into the cakes of commerce, and can be protected against bacterial changes even in hot climates by the incorporation of a small addition (0.05 per cent.) of paranitraniline.

China is the largest consumer of indigo, and a considerable amount of indigo is now produced in Manchuria. (See Indican, Isatin, and Woad.)

**Indigo Carmine**, or soluble indigo, prepared by treating a sulphuric acid solution of indigo with soda, is a blue powder soluble in water and used in dyeing.

**Indigo White**, the leuco-compound ( $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2$ ), is a white, crystalline powder obtained from indigo by processes of reduction, including the use of ferrous sulphate and caustic soda, or grape sugar and soda, or hydrogenation at from  $50^\circ$  to  $60^\circ\text{C.}$  in presence of a reduced nickel catalyst, and with the addition of sodium hydroxide. It is used in dyeing, by making use of processes which are capable of reconverting it into indigo blue on contact with the fabrics.

**INDIGO COPPER** — See Copper Sulphides.

**"INDIGOSOL O"** — A product described as a stable sulphonic acid ester salt produced from indigo white, which can be applied to the fibre in dyeing operations in exactly the same easy manner as indigo extract. It is completely soluble in water, and all kinds of wool, woollen yarn, and woollen materials are more easily dyed than in the vat.

**INDIUM (In) and its Compounds** — Atomic weight, 114.76. See Elements for other data. Indium is one of the less common elements, so named on account of the two lines it exhibits in the indigo-blue part of the spectrum; chemically analogous to aluminium, and occurring in many zinc-blendes. It is a ductile, soft, silver-white metal, easily

soluble in acids, and forms alloys with lead and thallium ; its compounds give a violet tinge to the Bunsen flame. Indium resembles aluminium in forming alums, and the halogen salts are soluble in water. The metal itself has found uses in bearings, packing material, jewellery, fluorescent glass, fusible metal, dental amalgam, collapsible tubes, moulds for plastics, electrical contact points, plating, and reflectors for light.

There are two **oxides**, namely, sesquioxide ( $\text{In}_2\text{O}_3$ ), and monoxide ( $\text{InO}$ ) ; a yellow **sulphide** ( $\text{In}_2\text{S}_3$ ) ; a **hydroxide** ( $\text{In}(\text{OH})_3$ ) ; three **chlorides**, namely, trichloride ( $\text{InCl}_3$ ), dichloride ( $\text{InCl}_2$ ), and monochloride ( $\text{InCl}$ ) ; a **bromide** ( $\text{InBr}_3$ ) ; an **iodide** ( $\text{InI}_3$ ) ; a **nitrate** ( $\text{In}(\text{NO}_3)_3 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ ) ; a **sulphate** ( $\text{In}_2(\text{SO}_4)_3$ ). (See C. L. Wilson and E. A. Peretti, on " Zinc-Indium Alloy System " (*Ind. Eng. Chem.*, **28**, 204 (1936)) ; C. L. Wilson and O. J. Wick, on " Cadmium-Indium Alloy System " (*Ind. Eng. Chem.*, **29**, 1164 (1937)) ; *Rarer Metals*, by J. DeMent and H. C. Dake (Chemical Publishing Co., Brooklyn, N.Y.) ; *Indium*, by Maria T. Ludwick (Indium Corp. of America, New York).)

**INDOLE or BENZOPYRROLE** ( $\text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4\text{NH}$ ) is regarded as the parent

substance of indigo, and is stated to occur in the essential oil of jasmine flowers. It is a feebly basic body of faecal-like odour, soluble in alcohol, ether, and hot water ; yields indigo when oxidized with ozone, and is used in perfumery. Both indican and indole at times result from protein decomposition in the bowels of man and other mammals.

**INDOPHENOLS** — A group of dyestuffs of phenolic character.

**INDUCED REACTIONS** — See Chemical Interactions.

**INDULINES** — A group of artificial dyestuffs made by condensing aminoazobenzene with aniline and aniline hydrochloride. They are manufactured as either spirit-soluble or water-soluble blue dyes.

**INDUSTRIAL ALCOHOL** — See Alcohol (Ethyl).

**INDUSTRIAL CHEMISTRY** — The processes of industrial chemistry are so many in number that their enumeration would be unduly long. Many of these are described in this work, and many excellent treatises discuss the processes in detail. Such treatises are *Roger's Manual of Industrial Chemistry*, by C. C. Furnas (D. Van Nostrand Co., New York) ; *The Chemical Process Industries*, by R. Norris Shreve (McGraw-Hill Book Co., New York) ; *Industrial Chemistry*, by Emil R. Riegel (Reinhold Publishing Corp., New York) ; and *Unit Processes in Organic Synthesis*, by P. H. Groggins (McGraw-Hill Book Co., New York).

**INDUSTRIAL DISEASES** — See Hazardous Chemicals, and Poisons.

**INERT GAS-SHIELDED ARC WELDING** — See " Heliarc " Welding.

**INFLAMMABILITY** — See Hazardous Chemicals, Dust and Dust Explosions, Flame, Flash-point, and Ignition.

**INFRA-RED SPECTROSCOPY** — Infra-red radiation consists of energy whose wave lengths are within the limits of 7,500 Å. (angstroms) and 350,000 Å. (see Wave Lengths). It is customary in speaking of infra-red radiation to express the wave length in microns ( $\mu$ ), where  $1\mu=10,000 \text{ Å.}=10^{-4} \text{ cm.}$ , and to speak of the frequency unit, wave number, as reciprocal centimetres ( $\text{cm.}^{-1}$ ), where  $1 \text{ cm.}^{-1}=\frac{1}{\lambda}$  ( $\lambda$ = wave length).

All radiation has a source for its energy, in the case of infra-red radiation it is due to oscillation of atoms within the molecules. The amplitude of these oscillations is extremely minute (about  $10^{-10} \text{ cm.}$ ) and the frequencies are high (about  $10^{14}$  cycles per second). Since these frequencies are of the same order of magnitude as those of infra-red radiations, some direct relationships might be expected to exist between the motions of the atoms within molecules and the absorption or emission of infra-red radiation.

Those molecular vibrations which are accompanied by a change of so-called "infra-red active" vibrations, absorb, by resonance, all or part of the incident radiation, provided the frequencies of the radiation coincide exactly with those of the intermolecular vibrations. Therefore, if a sample of a single kind of molecule is irradiated by a succession of monochromatic bands of infra-red radiation, and the percentage of radiation transmitted is plotted against either wave length or frequency, the resulting curve is a picture of the intermolecular motion. A detailed analysis of these curves indicates that although they appear complex they are merely summations of a number of simple oscillations or vibrations. Each simple vibration is referred to as a "fundamental" or "normal" mode of vibration. A normal mode of vibration is defined as a mode in which the centre of gravity of the molecule does not move, and in which all the atoms move with the same frequency and in phase. Each normal mode is independent of the others in that any one can occur without affecting the others. Thus it is possible to show mathematically that in any non-linear molecule of  $n$  atoms there are  $3n-6$  normal modes of vibration, whereas a linear molecule possesses  $3n-5$ . It is possible for all of these vibrations to occur simultaneously and yet have each mode retain its characteristic frequency. An analysis of an infra-red spectrum constitutes an analysis of the internal atomic mechanics of the molecule under observation.

The infra-red spectrometer, by measuring the frequencies of the infra-red radiation absorbed by a substance, reveals the characteristic mechanical frequencies of the molecules of the substance. Since the molecular frequencies are functions of the atoms themselves, as to spatial arrangement, valence forces, and intermolecular forces, the infra-red spectrometer is a valuable tool for the analytical and the theoretical chemist and physicist.

Although it is possible to calculate mathematically the normal modes of vibration for some simple molecules and thus elucidate their structure, the problem is as yet too complex to solve mathematically for

non-symmetrical molecules. For example, benzene is so symmetrical that, although it contains 12 atoms, only a fourth-degree equation is involved in the mathematical solution, but when its symmetry is destroyed as in ortho-chlorophenol a thirty-third-degree equation is required.

Most molecules of interest to the industrialist are complex, and it is often necessary or helpful to know something about their structure. Since the mathematical approach presents an improbable solution some other method is required to correlate the characteristics of the observed infra-red spectrum with the molecular structure. Considerable success in this line has been achieved by a purely empirical approach. The basis for this method consists in comparing the spectra of a large number of different molecules known to have a common atomic grouping. By the process of elimination it is often possible to find an absorption band whose frequency remains constant in each member of the series. If an unknown also shows this same absorption band it may reasonably be assumed that the particular atomic grouping is also present in the unknown.

In actual practice only a few observed bands can be assigned to given atomic groupings. For the majority of cases examined the observed bands are due to normal modes of vibration which are characteristic of the whole molecule. These general absorption bands are, however, very sensitive to structural changes, and may, therefore, furnish "fingerprints" of the molecules.

The normal vibrations of a molecule do not account for all the absorption bands in an infra-red spectrum. The far infra-red part of the spectrum is due to molecular-rotation or massive lattice vibrations of crystals. In the near infra-red overtones of the fundamental or normal mode vibrations are often found. Absorption bands also occur at frequencies which are equal to sums or differences (combination bands) of the fundamental bands. All these other bands in general absorb less strongly than do the fundamental ones. Since these other infra-red bands are so sensitive to the over-all molecular structure they can sometimes give a more accurate "fingerprint" of the molecule than the fundamental mode.

In general, for infra-red absorption the amount of light transmitted is related to the concentration by Beer's law (see same).

It is desirable to have a reference library of infra-red absorption curves for as many organic compounds as possible for the following reasons: first, they may be used to correlate molecular structure with spectral "fingerprints," second, to use in identifying unknown compounds, and third, to determine the possibility of qualitative and quantitative infra-red analysis of mixtures. There are available some reference libraries of infra-red absorption curves. Of course, these are incomplete and have their limitations, but are, nevertheless, useful.

*References:* *Infrared Spectroscopy*, by Barnes, Gore, Liddel and Williams (Reinhold Publishing Corp., New York); *Textbook of Physical Chemistry*, by Glasstone (D. Van Nostrand Co., New York); *Annual Reports of the Progress of Chemistry* (Chemical Society, London (1946

and 1945)); "Determination of Organic Functionality by Molecular Spectroscopy," by Coggeshall (*Anal. Chem.*, **22**, 381 (1950)); "Infrared Analysis of Phenol, Cresols, Xylenols and Ethylphenols," by Friedel, Pierce and McGovern (*Anal. Chem.*, **22**, 418 (1950)); and Wave Lengths.

**INFUSION** — An extract prepared by steeping or digesting vegetable substances or parts of plants in a solvent liquid with or without heating; sometimes effected by percolation.

**INFUSORIAL EARTH** — Light-coloured siliceous deposits found near Ebsdorf, also in the United States and elsewhere, are known by this name, but it is also applied to other deposits such as kieselguhr and diatomite, used as absorbents and for polishing purposes. (See Diatomite, Kieselguhr, and Tripoli.)

**INKS** — Liquids or pigments used for writing or printing, and made of various colours, such as black, blue, green, red, yellow, brown, and purple.

**Black Ink** is a mixture of an infusion of gall nuts with ferrous sulphate and a certain proportion of hydrochloric acid, also of gum arabic dissolved in the mixture to give body and gloss to the ink. Sometimes logwood and indigo carmine are added, and there are many recipes for its preparation.

Ordinary writing-ink stains can often be removed by alternate applications of a dilute solution of oxalic acid and that of bleaching powder.

**Blue Ink** can be prepared by dissolving Prussian blue in a dilute solution of oxalic acid. Condensation products of formaldehyde with phenols and their esters, which give a deep blue coloration with iron salts, are also used for making inks which have the advantage over iron gallate inks in that they do not favour the formation of rust, etc.

**Red Inks** are prepared from cochineal or Brazil-wood, or by dissolving carmine in ammonia solution. Some red ink stains can be removed by the use of perborate solutions.

**Indelible Ink** is prepared, amongst other methods, by mixing ordinary ink with Indian ink or lamp-black rubbed up with weak hydrochloric acid.

**Copying Ink** is prepared from logwood extract dissolved in vinegar and water, to which certain quantities of copper sulphate, alum, gum or glycerine, and sugar are added.

The formula adopted by the United States Government is as follows :

Tannic acid	..	..	..	..	46.8 grams
Gallic acid	..	..	..	..	15.4 "
Ferrous sulphate	..	..	..	..	60.0 "
Gum arabic	..	..	..	..	10.0 "
Dilute hydrochloric acid (U.S.P.)	..	..	..	..	50.0 "
Phenol	..	..	..	..	1.0 "
Suitable blue dye	..	..	..	..	4.4 "

and water to make up to 1,000 c.c. at 15.6° C.

The British Government's specification for inks requires a minimum of 0.2 per cent. iron for a fountain-pen ink and 0.5 per cent. for a standard ink for record purposes.

**Copying Pencils** are compounded of graphite, China clay, and some such dye as methyl violet.

**Cancelling Inks** must contain pigment and dyes of such character as to penetrate the fibre of paper so that the mark cannot be removed. They vary in composition, but lamp-black is often used in conjunction with a coal-tar dye and some non-drying oil.

**Ink for Glass and Tin** — Add a spirit-soluble dye to a 15 per cent. solution of shellac in alcohol, and apply with a pen.

**Sympathetic Inks** — The use of cobalt salts in the preparation of these inks is referred to under Cobalt Compounds, and resort is made to many other substances. For example, milk, orange or lemon juice, dilute sulphuric acid, saliva, urine, and soap suds can be used on unglazed paper for writing which remains invisible until heat is applied, when it becomes permanent. Messages written with a dilute solution of copper chloride become visible whenever the paper is warmed, while solutions of many metallic salts, such as lead acetate, can be used and made evident by exposure of the paper to hydrogen sulphide. If the paper be glazed, the pen must not be pointed, as it is liable to scratch away the glaze, thus rendering the scratches detectable either by a microscope or swabbing the surface with ink and then rubbing it off, the ink being absorbed by the unglazed portions.

When a strong solution of nitre is used for writing on paper, the writing must begin at a pre-arranged spot near the edge, and must be continuous, the application of a red-hot pin momentarily applied to the beginning of the writing causing a char, which runs right through the message.

The action of ink in developing writing made with lemon-juice or saliva is partly physical, as already explained, and partly chemical, increased absorption of pigment being one of the features, and acceleration of the oxidation of the ink being another feature.

The ultra-violet lamp is applied in many cases to discover secret messages by means of the fluorescence exhibited by many materials used in writing. (See Fluorescence.)

**Marking Ink** usually consists of silver nitrate solution coloured and thickened with gum, but many others consist of cresol and dyes of the aniline class. Such inks are used for marking cotton and other fabrics.

**Printing Inks** are made by incorporation of pigment with a suitable varnish medium and such other dryers and accessories as may be appropriate to their special applications. They are of great variety and of different materials, typographic inks being used for catalogues, book printing, etc., and made thinner and softer than lithographic inks (which must be unaffected by water), and special ones again being made for the higher quality of depressed surface printing. In the past they were made chiefly from lamp-black and linseed oil, soap and resin being sometimes incorporated; but lamp-black having become too expensive, it has been displaced by the use of resin black, soot, "shale," or other forms of carbon admixed with mineral matters and colouring matters such as aniline colours, or chromium, iron, or manganese compounds; while linseed and castor oils have also been largely displaced by tar

oils and mineral oils. For good and medium qualities, however, polymerized or boiled linseed oil is still used, together with resin oil, soap or resin soap, and various pigments. Bitumen, asphalt, or stearin pitch are also used in admixture in some inks, particularly those used for rotary press work, as they improve the covering property and prevent the ink piercing the paper. For news-press work carbon black as produced by the incomplete combustion of natural gas is used because it has great tinctorial strength, but in order to prevent any brownish undertone in the thin film of ink used, a little bluish dye is added to correct the colour and intensify the effect; mineral oil and resin being the usual blend employed, the whole being mixed and finely ground. "Sulphite" waste liquor is used in Sweden as a thickening agent for printing inks, and genuine "quicksilver vermilion" is used in the manufacture of red printing ink. (See *Printing Inks, Their Chemistry and Technology*, by Carleton Ellis (Reinhold Publishing Corp., New York).)

**Typewriting Inks** are intermediate between writing and printing inks, aniline dyes being often employed in conjunction with the other materials, which sometimes include a proportion of glycerine.

**Chinese Ink** is made from vegetable charcoal prepared from rice straw or vegetable oils and other suitable materials.

**Indian Ink** is a black powder imported from China, made from carbon prepared by burning camphor, cemented with gelatine or glue.

**Invisible Ink** — See paper by H. T. F. Rhodes on "The Scientific Examination of an Historic Document," dealing with the inks used in preparing and making some part illegible (*Chem. and Ind.*, **50**, 303 (1931)); article on Writing Materials in *Pharmaceutical Formulas*, vol. 11 (The Chemist and Druggist Press, London); *Inks*, by C. Ainsworth Mitchell (Chas. Griffin and Co., London); *Ink Manufacture*, by S. Lehner (Scott, Greenwood and Son, London); and Sympathetic Inks above.

**INORGANIC CHEMISTRY** — The term "inorganic" is applied to all substances that do not contain carbon as a constituent, also to some few others in which carbon is present in an unimportant sense, such as the metallic carbonates. The natural rocks and earths, the metals and minerals, are all inorganic bodies. (See *Textbook of Inorganic Chemistry*, by G. S. Newth (Longmans, Green and Co., London); *Textbook of Inorganic Chemistry*, by A. F. Holleman (Chapman and Hall, London); *Applied Inorganic Analysis*, with special reference to metals, minerals, and rocks, by Hillebrand and Lundell (Chapman and Hall, London); *Manual of Chemical Analysis (Qualitative and Quantitative)*, by G. S. Newth (Longmans, Green and Co., London); *The Quantitative Analysis of Inorganic Materials*, by N. Hackney (C. Griffin and Co., London); *Technical Chemists' Handbook: Tables and Methods of Analysis for Manufacturers of Inorganic Products*, by G. Lunge (Gurney and Jackson, London); *Elementary Inorganic Chemistry*, by J. W. Mellor (Longmans, Green and Co., London and New York); *Modern Inorganic Chemistry*, by J. W. Mellor (Longmans, Green and Co., London and

New York); *A Textbook of Inorganic Chemistry*, by J. R. Partington (Macmillan Co., London and New York); *Inorganic Chemistry*, by T. M. Lowry (Macmillan Co., London and New York); *Comprehensive Treatise on Inorganic and Theoretical Chemistry*, in 16 volumes, "the most complete source of information existing in English," by J. W. Mellor (Longmans, Green and Co., London and New York); *A Textbook of Inorganic Chemistry*, in 22 parts, edited by J. Newton Friend (Chas. Griffin and Co., London); *General Inorganic Chemistry*, by M. C. Sneed and J. L. Maynard (D. Van Nostrand Co., New York); *Principles of Chemistry and Reference Book of Inorganic Chemistry*, by W. M. Latimer and J. H. Hildebrand (The Macmillan Co., New York); *Modern Aspects of Inorganic Chemistry*, by H. J. Emeleus and J. S. Anderson (D. Van Nostrand Co., New York); *The Chemical Elements and Their Compounds*, by N. V. Sidgwick (Oxford University Press.).

**INOSITOL (Inosite)** ( $C_6H_8(OH)_6$ ) — A crystalline substance found in various animal tissues. It melts at  $225^\circ C.$ , and is not susceptible to alcoholic fermentation. It forms part of certain enzyme systems and in 1940 was shown by Woolley to be essential to mice, which develop alopecia in its absence. (See Vitamins.)

**INSECTICIDES** — Substances used for killing insects, and classified according to their mode of action as contact insecticides, fumigants, and stomach—or internal—poisons. From a chemical point of view, however, it is more convenient to group insecticides into three classes, namely, inorganic compounds, plant products, and synthetic organic compounds.

Many of the older insecticides were inorganic compounds which functioned as stomach poisons. These materials are applied to the plant surface or in bait mixtures, and exert their toxic action after ingestion by the insect. Such materials include Paris green, lead arsenate, calcium arsenate, and magnesium arsenate, all of which are used to control insects attacking fruit and vegetable crops. Lead arsenate is widely used against the codling moth of apples, and calcium arsenate against the cotton boll weevil. "Sodium arsenate" (actually arsenite), made by dissolving arsenious oxide in sodium hydroxide, is used in poison baits to control grasshoppers and locusts.

Various inorganic compounds of fluorine have been used as insecticides, including cryolite, several fluosilicates, and sodium fluoride. The last is a common constituent of roach powders. Other inorganic insecticides which have found limited use are borax (sodium borate), thallium sulphate (in ant poisons), and tartar emetic (potassium antimony tartrate). Practically all of the inorganic insecticides are highly toxic to animals, and they should be used with caution on food crops, where the presence of poisonous residues may constitute a health hazard.

Most of the plant products function as contact insecticides; *i.e.*, they must be applied directly to the insect to exert their killing power. One of the oldest and most widely known plant products used for insecticidal purposes is nicotine, derived from the tobacco plant. Several million

pounds of nicotine are used annually for pest control. Anabasine, a compound closely related to nicotine, and produced from *Anabasis aphylla* is considered to be approximately as effective as nicotine as an insecticide. Nicotine and anabasine are highly toxic to all forms of animal life.

Rotenone, the active principle of a group of tropical leguminous fish poison plants, is widely used as an insecticide. Rotenone is found in the roots of *Derris* (tuba), *Lonchocarpus* (cube), *Tephrosia*, and *Mundulea* species, and insecticidal sprays and dusts are prepared from the ground roots or extracts therefrom. Several compounds related to rotenone have been isolated from the fish poison plants, and some of these are toxic to insects.

The flower heads of pyrethrum (*Chrysanthemum cinerariaefolium* D.C.) contain substances which are highly toxic to insects. Staudinger and Ruzicka isolated the active principles, which were found to be esters. More recent work indicates that there are at least four of these esters, designated as pyrethrin I, pyrethrin II, cinerin I, and cinerin II. Pyrethrum is prepared for insecticidal use by drying the flower heads, and grinding or extracting them with an organic solvent. Extracts or pyrethrum flowers dissolved in light hydrocarbon oils are widely used as household sprays to control flies, gnats, and mosquitoes. "Flit" and many other proprietary sprays are prepared in this way. Both rotenone and pyrethrum insecticides have the decided advantage of being relatively non-toxic to higher animals, hence they are commonly used on fruits and vegetables intended for human consumption. Other plant products less frequently used as insecticides include quassia, croton, larkspur, sabadilla, and hellebore.

Petroleum and other oils are useful insecticides, and large quantities are used for this purpose. The petroleum and tar oils are efficient contact poisons, and are frequently used as "dormant" sprays on fruit trees to destroy insect eggs.

Fumigants are insecticides which exert their action in the gaseous state. Naphthalene and paradichlorobenzene are commonly used in homes to protect woollens and silks from attack by the clothes moth. These are available as "moth balls," "moth crystals," etc. In houses, warehouses, flour mills, ships' holds, and other confined spaces fumigants such as hydrocyanic acid, methyl bromide, carbon disulphide, ethylene dichloride, and others are used to eradicate insects. The structure to be fumigated must be closed tightly for maximum effect.

Within the past few years a large number of synthetic organic compounds have been found to possess high toxicity to insects. Probably the most widely used of these is D.D.T. (1,1-(bis-*p*-chlorophenyl)-2,2,2-trichloroethane). This compound was discovered to have remarkably high toxicity to a number of species of insects in 1939, although the compound itself had been known for many years. Very minute amounts of D.D.T. suffice to kill many insects, and it retains its toxicity over long periods of time, so that a housefly, for example, may be killed by walking over a light deposit of D.D.T. on walls, screens, or other surfaces several months after the surface has been treated.

D.D.T. seems to be most effective in controlling those insects which attack man and animals, such as flies, mosquitoes, fleas, and lice, but is toxic to many others as well. It may be dissolved in a suitable organic solvent and applied as a spray, or diluted with an inert substance and used as a dust. D.D.T. is toxic to most animals, and may be absorbed through the skin from solutions, hence care should be exercised in using the compound.

Other synthetic organic chemicals which have been found to be efficient insecticides include the gamma isomer of hexachlorocyclohexane (benzene hexachloride; "Gammexane"); tetraethyl pyrophosphate ("TEPP"), various organic thiocyanogen compounds, and many others too numerous to mention. It is probable that these materials will each find a useful place in pest control operations when their particular advantages and limitations have been thoroughly investigated.

*References:* *Chemistry of Insecticides and Fungicides*, by D. E. H. Frear (D. Van Nostrand Co., New York); *The Scientific Principles of Plant Protection*, by H. Martin (E. Arnold, London); *The Chemistry and Toxicology of Insecticides*, by Shepard (Burgess Publishing Co., Minneapolis); *Spray Chemicals and Application Equipment*, by McClintock and Fisher (Horticultural Press); *D.D.T.*, by Campbell and West (Chapman and Hall, London); *Annual Reports of the Progress of Applied Chemistry* (Society of Chemical Industry, London); *A Survey of Insecticide Materials of Vegetable Origin* (Imperial Institute, London); *Chemistry and Uses of Insecticides*, by E. R. de Ong (Reinhold Publishing Corp., New York); *Chemical Insect Attractants and Repellants* (Blakiston Co., Philadelphia); see also "Deenate," "Lexone," "Loro," Methoxychlor, Fungicides, Moth-Proofers, Nicotine, Pyrethrum, and Rotenone.

**INSTRUMENTATION** — The selection and arrangement of instruments by which the variables of a process are measured, recorded, and controlled. Important variables include temperature, pressure, rate of flow, liquid level, and chemical compositions (e.g., the pH value of a liquid or the CO<sub>2</sub> content of a gas), all of which can be controlled automatically. Controllers are supplied to give various kinds of response, such as on-off, proportional, proportional with reset, with rate response, or with both. The most suitable type of response depends on the nature of the system to be controlled. The choice of instruments having appropriate characteristics is increasingly important in chemical industry.

*References:* T. J. Rhodes, *Industrial Instruments for Measurement and Control* (McGraw-Hill Book Co., New York); D. E. Eckman, *Principles of Process Control* (John Wiley and Sons, New York); *Instrument and Process Control* (New York State Vocational and Practical Arts Association).

**INSULATING MATERIALS** — Electrical insulating materials used for various applications include asbestos, "glass silk," rubber, ebonite, "Bakelite," and other synthetic resins, bitumen, shellac, certain

those found by the latter. The interfacial tensions of pure liquids in contact with water are constant at one temperature, and are the less the greater their mutual solubility.

#### INTERFACIAL TENSION BETWEEN SOME PAIRS OF IMMISCIBLE LIQUIDS

Pairs of Liquids	Number of Drops at 20° C. (Inversely Proportional to Surface Tension)
Water—Linseed oil, raw .. .. .	55
Water—Linseed oil, 90 per cent., with linseed oil	
fatty acids, 10 per cent. .. .. .	90
Water—Linseed oil, 80 per cent., with linseed oil	
fatty acids, 20 per cent. .. .. .	225

**INTERMEDIATES** — A general term for some hundreds of derivatives obtained from anthracene, benzene, cresols, naphthalene, phenol, toluene, and other direct coal-tar products, mostly colourless, but all of which are used in the manufacture of synthetic dyes or drugs. They include H acid, aniline oil, dinitrochlorobenzene, dinitrophenol, ortho- and para-chloraniline, naphthol (alpha and beta), para-chlorophenol, para-nitro-ortho-aminophenol, naphthylamines, phthalic anhydride, anthranilic acid, ortho-aminobenzoic acid, dimethylaniline, nitrobenzene, para-nitraniline, resorcinol, salicylic acid, many aromatic aldehydes, and a large number of other compounds, many of which are described under their respective names. (See *Intermediates*, by A. Davidson (Ernest Benn, Ltd., London); comprehensive list of "Trade Names and Formulas of Dyestuff Intermediates" in *Handbook of Chemistry*, by N. A. Lange (Handbook Publishers, Inc., Sandusky, Ohio, U.S.A.); also *Dyes, and Acids*.)

**INTROFIERS** — Substances that accelerate impregnation, that is, when added to impregnating media cause changes in their fluidity and specific wetting qualities. (See *Wetting Agents*.)

**INULIN or ALANT STARCH** ( $C_6H_{10}O_5$ )<sub>x</sub> — A carbohydrate contained in dahlia bulbs (*Dahlia variabilis*) to the extent of about 10 per cent. of the weight of the ripe tubers, and in smaller proportions in the roots of other members of the Compositæ, such as chicory and artichokes.

Fructose is the only product of hydrolysis of inulin, and fructose is made from inulin on a semi-commercial scale. The structural unit has been shown to be fructofuranose. End-group assay shows that the molecular weight is about 5,000, and the molecule contains about 30 units. (See *An Introduction to the Chemistry of Carbohydrates*, by Honeyman (Clarendon Press, Oxford).)

In the pure state inulin is a white, crystalline powder resembling starch, but, unlike that substance, it dissolves in aqueous sodium hydroxide and in hot water to a clear solution, and is not coloured blue by iodine. It is unaffected by diastase, and is not fermentable by yeast, but when boiled with water or dilute acid it is hydrolysed to fructose. It is used in the preparation of diabetic bread, and is a stronger sweetener than cane sugar.

“ **INVAR** ” — A nickel-steel alloy (36 per cent. nickel) devoid of temperature coefficient of expansion, so that surveying tapes made of it are almost unaffected by temperature ; also used for making the pendulum rods of good clocks.

**INVERSION** — See Invertase, Sugar (Sucrose), and Walden's Inversion.

**INVERTASE (Invertin, Zymase)** — An enzyme present in ordinary yeast, which, apart from the yeast cells themselves, has the power of converting (inverting) cane sugar into glucose and fructose by hydrolysis to the reported extent of 200,000 times its own weight of cane sugar without then losing its effect  $(C_{12}H_{22}O_{11}(\text{sucrose}) + H_2O = C_6H_{12}O_6(\text{glucose}) + C_6H_{12}O_6(\text{fructose}))$ .

It is ordinarily prepared by macerating yeast which has been dried at room temperature (in order to break the cell walls) with water, and filtration of the extract, using an ordinary filter-paper, so as to retain the yeast cells thereon. It is stated to decompose gradually in aqueous solution, and to lose all its activity in course of about eighteen months, also to undergo a temporary loss of activity on drying.

The hydrolysed product “invert sugar” is lævo-rotatory, whereas a solution of cane sugar is dextro-rotatory, the fructose being more strongly lævo-rotatory than the glucose is dextro-rotatory—an instance of inversion of optical rotation. Its commercial manufacture is carried out by gently boiling for some thirty minutes a mixture of 750 pounds sucrose in 250 pounds water and 10 ounces of tartaric or 13 ounces citric acid, the sugar being first dissolved in the water, and the acid (also dissolved in water) being added afterwards. The finished product should weigh 950 pounds (S. Jordan).

**INVERT SUGAR** — See Invertase.

**IODATES** — See Iodine Compounds.

**IODIC ACID** — See Iodine Compounds.

**IODIDES** — See Iodine Compounds.

**IODINE (I) and its Compounds** — Atomic weight, 126.92. See Elements for other data. Iodine, in combination with potassium, sodium, magnesium, and calcium, is widely distributed in nature in small percentages. It is also present in sea-water, sea-weeds (including the *phyllophoren* algæ of the Black Sea), and *caliche* or Chile saltpetre. (See Caliche.) It is prepared to some extent from kelp (ashes from sea-weeds), also from the soluble iodides found in many of the mineral springs of the Dutch East Indies and, to some extent, as a by-product in superphosphate manufacture in Denmark, the iodine source being the phosphate rock employed. The main supply came from the concentrated mother-liquor of the Chile saltpetre (which contains less than  $\frac{1}{4}$  per cent.), and that of the Stassfurt salt deposits, from the iodate content of which it is precipitated by sodium bisulphite, and, after drying, purified by sublimation. The oil-wells of California now furnish a principal source of iodine (see “New American Iodine Industry,” by G. Ross Robertson (*Ind. Eng. Chem.*, 26, 376 (1934))). In

Russia, iodine is produced to some promising extent from the same source, the well-waters containing some 0.015 to 0.2 gram per litre. There is also a considerable production in liquid form from natural sources in Indonesia.

The sea-weeds which contain most iodine are of the so-called "drift" order—viz., *Laminaria digitata* and *L. stenophylla*, each of which has been stated to contain a little less than  $\frac{1}{2}$  per cent., and the ash of the root of *L. hyperborea* about 1 per cent., the stalks about 3 per cent., and that of the leaves about 4 per cent. iodine. The weeds of the White Sea and the Murman and Brittany coasts are rich in iodine content. A mixture of various Black Sea algæ contained 0.0859 to 0.172 per cent. iodine or 0.138 to 0.338 per cent. of the ash after combustion, while the corresponding figures for *Cystosieæ* are 0.095 and 0.146 per cent., and for *Phyllophora* 0.645 and 1.01 per cent. (Komareckyj, *B.C.A.*, B, 1929, 355). The iodine contents of other sea-weeds are given as follows: *Fucus vesiculosus* and *nodosus*, 0.070 per cent.; *Fucus vesiculosus*, 0.013 per cent.; *Potwrack*, 0.050 per cent.; *Laminaria*, 0.175 per cent.; *Costaria*, 0.029 per cent.; *Alaria*, 0.027 per cent. (See Kelp, and Seaweeds.)

Iodine organic products of therapeutical value are also made in France from the sea-weed *Laminaria flexicaulis*. (See Algin.)

Details of the manufacturing processes for obtaining iodine from Chile saltpetre and sea-weeds are given in G. S. Newth's *Textbook of Inorganic Chemistry* (Longmans, Green and Co., London and New York.).

Iodine is blue-black, of sp. gr. 4.93, easily obtained in crystalline form, and readily vaporizes, the vapour having a beautiful violet colour; it has a characteristic penetrating odour and is only slightly soluble in water, but readily soluble in a solution of potassium iodide, in alcohol, in carbon disulphide, in chloroform, in ether. Even an extremely dilute solution of iodine gives with starch solution an intensely blue-coloured product. In general properties it strongly resembles its family neighbours, chlorine and bromine. Dilute solutions of it in water and alcohol are used in surgery for antiseptic purposes.

Iodine in combination with the alkaline metals forms **iodides**, the most valuable of which is potassium iodide (KI), which is produced in solution together with potassium iodate when iodine is dissolved in a warm solution of potassium hydroxide. Potassium iodide crystallizes in anhydrous cubes, is very soluble in water, and is extensively employed as a medicament in the treatment of goitre, etc., and in photography. Iodine is concerned with nutrition of the human body, the thyroid gland being the mechanism controlling exchange, and remarkable results have been achieved by the use of iodine for prevention of goitre.

**Hydriodic Acid (HI)** can be prepared in a variety of ways, and among others by exposing a mixture of hydrogen gas and iodine vapour to strongly heated platinum sponge; also by adding to 10 parts of iodine in an atmosphere of carbon dioxide, 1 part of phosphorus little by little slowly, and pouring upon the mixture 4 parts of water, when upon the application of gentle heat an abundance of hydriodic acid gas is

generated free from iodine. An excellent laboratory method of preparation is that of passing hydrogen sulphide into a suspension of iodine in water. When the iodine has been transformed into hydriodic acid, the precipitated sulphur is filtered off, and the solution subjected to distillation for the recovery of pure hydriodic acid. The gas is colourless, pungent, and extremely soluble in water, a solution of 45 per cent. strength having a sp. gr. of 1.476.

**Iodic Acid** ( $\text{HIO}_3$ ) is a crystalline, white, solid body, of m.p.  $110^\circ \text{C}$ ., soluble in water; prepared by action of sulphuric acid upon barium iodate, which is made by reaction of iodine and barium hydroxide solution; or by the reaction of potassium chlorate and iodine ( $2\text{KClO}_3 + \text{I}_2 = 2\text{KIO}_3 + \text{Cl}_2$ ). It forms iodates, such as potassium iodate ( $\text{KIO}_3$ ), corresponding to potassium chlorate ( $\text{KClO}_3$ ).

**Periodic Acid** ( $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$  or  $\text{H}_5\text{IO}_6$ ) is a white, dibasic, crystalline acid made by action of perchloric acid upon iodine; it melts with decomposition at  $140^\circ \text{C}$ ., is soluble in water and alcohol, and is used as an oxidizing agent.

**Iodine Pentoxide** ( $\text{I}_2\text{O}_5$ ) is a white, crystalline body, soluble in water, and when heated to  $275^\circ$  to  $300^\circ \text{C}$ . is split up into iodine and oxygen.

Iodine forms two compounds with chlorine, **trichloride** ( $\text{ICl}_3$ ) and **monochloride** ( $\text{ICl}$ ). Both these compounds are formed by passing dry chlorine gas over iodine, when it first of all melts to a dark reddish-brown colour, and subsequently solidifies to a mass of red crystals of  $\text{ICl}$  if care be taken not to use an excess of chlorine; but if more chlorine be used, then the yellow trichloride in crystalline form is produced.

**Iodine Cyanide** ( $\text{ICN}$ ) is a colourless, crystalline substance of pungent odour, soluble in water, alcohol, and ether; used as a preservative by taxidermists.

**IODINE VALUE or NUMBER (Fats and Oils)** — See Fats.

**IODITE (Iodyrite)** — Mineral silver iodide, of crystal system No. 3, and sp. gr. 5.5. (See Silver.)

**ODOFORM** ( $\text{CHI}_3$ ) — A yellow, crystalline substance prepared by warming alcohol with iodine and alkali, or by heating acetone, acetaldehyde or isopropyl alcohol with iodine in presence of an alkali.

It is sparingly soluble in water; slightly soluble in alcohol; soluble in ether and chloroform; m.p.  $120^\circ$  to  $122^\circ \text{C}$ ; and has a penetrating odour. It has only weak bactericidal properties, but exerts an antiseptic action when applied to wounds, possibly due to the liberation of iodine.

**IODOPHTHALEÏN (Iodophthaleïn Sodium)** ( $\text{C}_{20}\text{H}_8\text{O}_4\text{I}_4\text{Na}_2 \cdot 3\text{H}_2\text{O}$ ) — A blue, crystalline powder, being the disodium salt of tetraiodophenolphthaleïn, obtained by iodination of phenolphthaleïn; soluble in water; slightly soluble in alcohol. Iodophthaleïn is opaque to X-rays and, after oral administration, it is excreted by the liver into the gall bladder. It is used in medicine, therefore, for visualization of the gall bladder. In some cases, a sterile, fresh solution may be administered by intravenous injection for the same purpose.

K.C.E.—19

**IODOPYRACET INJECTION** — See Diodone Injection.

**IODOXYL** ("Pyelactan," "Uropac," "Uroselectan-B," "Urumbrian-B") ( $C_8H_3O_5NI_2Na_2$ ) — A white, odourless powder, being the disodium salt of *N*-methyl-3,5-diiodo-4-pyridone-2,6-dicarboxylic acid; freely soluble in water; slightly soluble in alcohol (90 per cent.); insoluble in chloroform and ether; m.p. about  $174^\circ C.$ , with decomposition. It is prepared by condensing together acetone and ethyl oxalate, hydrolysis of the resulting ethyl ester of chelidonic acid, treatment with ammonia to form chelidamic acid, iodination and methylation of the diiodochelidamic acid and subsequent conversion to the disodium salt. It is administered by intravenous injection for X-ray visualization of the kidneys and urinary tract. (See Diodone Injection.)

**IONAMINES** — A class of dyestuffs, being soluble amino- $\omega$ -methylene sulphonates such as  $C_6H_5 \cdot N_2 \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot SO_3Na$  (which can be rendered insoluble by hydrolysis), of value for dyeing artificial acetate silk, etc. They fix themselves upon this fabric and leave the cotton white when used in respect of a mixture of the two materials. (See Dyes.)

**ION EXCHANGE** — In practice the exchange of ions is between (1) a solution bearing the ions to be removed, and (2) a solid containing the ions for exchange—its own ions going into the solution and those of the solution going into the solid. For "hard" water containing calcium ions ( $Ca^{++}$ ) from either bicarbonate ( $Ca(HCO_3)_2$ ) or sulphate ( $CaSO_4$ ) the passage of the water through sodium zeolite ("NaZ") will exchange  $Ca^{++}$  ions for  $Na^+$  ions. Thus, by the removal of  $Ca^{++}$  ions the water is softened, but each  $Ca^{++}$  ion is replaced in the water by  $2Na^+$  ions. This is a chemical—not a catalytic—effect, and the amount of the exchange is dependent upon the total amount of exchanger available. When the exchanger is spent it is revived by passing a current of sodium chloride solution through it, and the reverse reaction takes place (sodium zeolite re-formed for use again and artificial hard water discarded).

Ion exchangers are specific, as the above example illustrates, where bicarbonate ions ( $HCO_3^-$ ) or sulphate ions ( $SO_4^{--}$ ) remain in the water—only the  $Ca^{++}$  ions and  $Na^+$  ions exchange. There are other exchangers that replace metallic ions, such as  $Ca^{++}$  or  $Na^+$ , by hydrogen ions ( $H^+$ ), in which case initial calcium sulphate hardness would result in an equivalent amount of sulphuric acid being present in the final water. To replace the sulphate ions ( $SO_4^{--}$ ) by hydroxyl ions ( $OH^-$ )—leaving the  $H^+$  ions and  $OH^-$  ions to form water—is possible by the use of anion exchangers. These are certain synthetic resins, and their use, after the metallic ions have been replaced by  $H^+$  ions, results in the complete "demineralization" of the water (distilled water quality).

The purification of commercial sugar solutions (beet, corn, fruit) is being accomplished by the use of ion exchangers. This is possible because sugar itself does not ionize, and the ion constituents of the commercial syrups can be removed by exchangers. The quality of the sugar solution is raised, more sugar is recovered, and there is less

molasses for disposal. Many other fields of application have been suggested, among which are the recovery of various metals from their waste salt solutions, the purification of vitamin and aminoacid preparations, the stabilization of milk for evaporation, and the removal of formic acid from formaldehyde solutions. (See *Ion Exchange—Theory and Application*, by F. C. Nachod, editor (Academic Press, New York).)

**IONIUM** — A radioactive substance, obtained as a disintegration product from uranium minerals, giving a spectrum and exhibiting chemical properties identical with those of thorium. According to G. D. Kammer and A. Silverman, it can be extracted from high-grade carnotite (containing more than 15 per cent. uranium oxide) with hydrochloric acid, and it exists in average Colorado carnotite in the proportions of 1 : 15.8 thorium, which is isotopic with ionium. (See Nuclear Chemistry.)

**IONIZATION** — (1) The charging of gaseous molecules so that the gas conducts an electric current. (2) Electrolytic ionization (dissociation), or splitting up of electrolytes in solution into two parts (anions and cations). (3) Atomic ionization is effected by the action of radiations. (See Electricity (Electrical Aspects), and Nuclear Chemistry.)

**IONONE** ( $C_{15}H_{20}O$ ) — An artificial essence of violet, made from citral and acetone: sp. gr. 0.935 to 0.940; b.p. at 10 m.m.,  $126^{\circ}$  to  $128^{\circ}$  C.; ref. ind. at  $20^{\circ}$ , 1.5035 to 1.5070; and opt. rot.,  $0^{\circ}$ . There are several so-called ionones, one of which is the odorous principle of the iris root. (See Irone, Orris Oil, and Perfumes.)

**IONS** — Electrified atoms or groups of atoms, produced by electrolytic dissociation of liquids or gases (as, for example, by the passage of X-rays). Solutions in water of salts and so-called "strong" acids (e.g., HCl,  $H_2SO_4$ ,  $HNO_3$ ) and bases (e.g., NaOH, KOH,  $Ca(OH)_2$ ) contain ions equally charged positively and negatively. Crystals of salts are made up of lattices of positively and negatively charged ions. (See Electricity (Electrical Aspects).)

**IPECACUANHA** — The dried root of *Cephaelis Ipecacuanha*, a small plant belonging to the Rubiaceæ growing in Brazil, Selangor, Bengal, and Burma. It contains from 2 to 3 per cent. of total alkaloids of which about 60 to 70 per cent. is emetine (cephæline monomethylether) and about 26 per cent. is cephaeline. The drug is used in medicine as an emetic, expectorant, and diaphoretic. (See Emetine.)

**IRIDIUM (Ir) and its Compounds** — Atomic weight, 193.1. See Elements for other data. Iridium is a white, hard, brittle, and lustrous metal, occurring in alloy form with platinum and osmium, in several Uralian ores, and nearly related to those metals in its chemical characters. Two of these alloys are known as platiniridium and osmiridium.

It is used in alloy with platinum for hardening, also in making fountain-pen points, magneto-point contacts, watch and compass bearings, and platinum-iridium alloy for use in thermocouples, etc. In compact form, iridium is insoluble in acids, and it forms alloys with copper, gold, lead, and mercury.

A number of compounds are known, including two **oxides**, namely, the sesquioxide ( $\text{Ir}_2\text{O}_3$ ), and the dioxide ( $\text{IrO}_2$ ), used as a pigment for china ware; three **chlorides**, namely, the tetrachloride ( $\text{IrCl}_4$ ), the trichloride ( $\text{IrCl}_3$ ), and possibly a dichloride ( $\text{IrCl}_2$ ); and two **iodides**, namely, the tetraiodide ( $\text{IrI}_4$ ), and the triiodide ( $\text{IrI}_3$ ).

Iridium salts are soluble in water; and, in common with palladium, the metal has the property of adsorbing gases by occlusion. (See Occlusion, and Osmiridium.)

**IRIS** — See Perfumes, and Irone.

**IRISH MOSS** (Carrageen) — The sun-dried (bleached) *Chondrus crispus*. (See Sea-weeds.)

**IRON** (Fe) and its Compounds — Atomic weight, 55.85. See Elements for other data; and also accompanying Charts. Iron occurs in nature in the form of pyrite and many other ores. Magnetic iron ore (*magnetite* or *loadstone*) ( $\text{FeO}, \text{Fe}_2\text{O}_3$ ) is a crystalline compound of oxides of iron, from which much of the best Swedish iron is made. Red *hematite* ( $\text{Fe}_2\text{O}_3$ ) (crystal system No. 3, and sp. gr. 4.5 to 5.4) is largely mined in some parts of Lancashire, Cumberland, and to some extent in Cornwall, while large deposits exist near Bilbao in Spain and elsewhere, especially in the Lake Superior region of Minnesota, which region produces about 75 per cent. of the ore used in the United States. Most of the remainder is produced in Michigan and in Alabama, that in Alabama having the advantage of being practically self-fluxing. The ore used in the United States contains an average of about 50 per cent. iron. Deposits of iron ore of considerable promise have been located in South Africa and in the Apuan Alps, between Massa and Lucca, the latter being a hematite containing nearly 42 per cent. iron.

Brown hematite ( $2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$ ), a hydrated oxide of iron, is the source of much of the iron made in France and Belgium, whilst large quantities of *spathic ore* (*siderite*) or *clay ironstone* (which is an impure carbonate of iron containing about 33 per cent. of iron, and the poorest of the iron ores that are worked) are used in England as a source of iron. Iron occurs as carbonate in the forms of *blackband* of the Scotch coalfields, and in an impure form in the neighbourhood of Northampton and the county of Oxfordshire.

Large deposits of micaceous iron ore (known also as *specular iron ore* and *iron glance*) are found in Brazil, and two mines are producing this form of hematite in Devonshire. Large deposits of hematite ore are known to exist upon certain islands on the eastern coast of Hudson Bay, whilst the Lorraine district is said to contain an iron ore reserve, in the nature of a brown hematite, very rich in phosphorus, of about 1,800,000,000 tons. Labrador deposits are expected to furnish iron ore when transportation arrangements are completed. It is reported that the greatest find of iron ore in recent times is that of U.S. Steel Company, whose ore claims at Cerro Bolivar, Venezuela, promise to equal the Lake Superior deposits in importance.

There are also mineral deposits of hydrated iron oxide or *bog-iron ores*, one of which is known as *limonite*, and of a hydrated basic sulphate

**IRON-CONTAINING SUBSTANCES**  
**CHARTS SHOWING PRINCIPAL APPLICATIONS**  
 Arranged by the Editor.

**CHART I. OF NATURAL OCCURRENCE**

**Principal Uses**  
 Paint pigments  
 Abrasives  
 Structural materials  
 Machinery  
 Apparatus  
 Transportation

**IRON ELEMENT**  
 4.5% of the earth's crust

Or, when expressed as oxides,  
 about 2.7%  $\text{Fe}_2\text{O}_3$   
 plus 3.4%  $\text{FeO}$   
 in the earth's crust

As Iron Oxide (principally)  
 Hematite ( $\text{Fe}_2\text{O}_3$ )  
 Limonite (Hydrated  $\text{Fe}_2\text{O}_3$ )  
 Magnetite ( $\text{Fe}_3\text{O}_4$ )  
 Franklinite ( $\text{Fe, Mn, Zn}$   
 oxides)

As Iron Disulphide (principally)  
 Pyrite ( $\text{FeS}_2$ )

As Ferrous Carbonate (princi-  
 pally)  
 Siderite ( $\text{FeCO}_3$ )  
 As Iron, Manganese Tungstate,  
 Wolframite

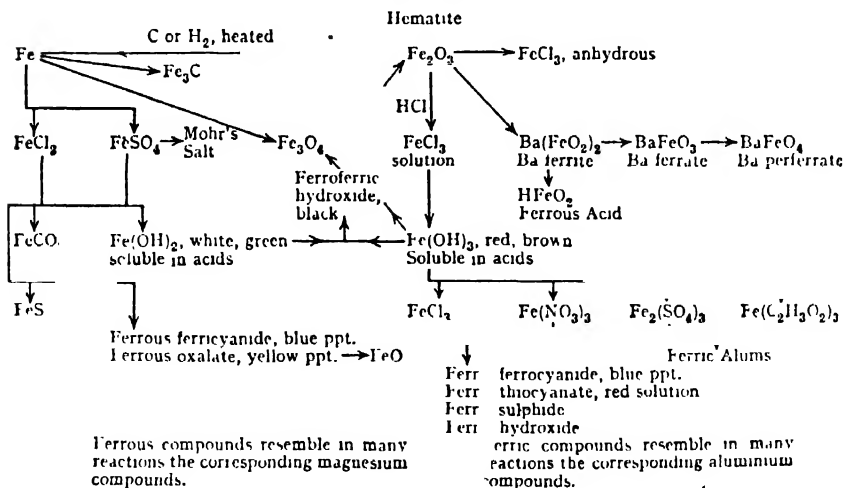
As Iron  
 Meteorites

As Iron Silicates (complex)  
 Igneous and their Metamor-  
 phosed Rocks  
 Sedimentary and their Meta-  
 morphosed Rocks  
 Soil  
 Clay

Most of the colour of rocks and  
 soils is due to the presence of  
 iron compounds, thus,  
 Ferric is red, brown, or yellow  
 Ferrous is green  
 Ferroferric is black

"In some respects iron stands  
 alone among the elements."  
 CAVEN AND LANDER.

**CHART II. OF MANUFACTURE**



of iron and potash known as *jarosite*, in Australia. Chromium iron ores come largely from New Caledonia, Rhodesia, the U.S.A. and Canada.

**Iron Ore Resources of the World** was prepared by the Ninth International Geological Congress, Stockholm, 1910.

**Beneficiation** of iron ore is practised, in order to concentrate low-grade ores into those of higher grade, by washing, jigging, tabling, and magnetic and density separation. Fine ores are agglomerated or sintered into lumps. Approximately one-fourth of the iron ore shipped from mines in the U.S.A. is beneficiated.

Iron as manufactured and dealt in commercially is not a pure metal, and varies very much in composition and qualities according to the purposes to which it is to be applied. The purest form of commercial iron is the fine malleable quality of which wire is made. Some of the better-known kinds of iron are named cast iron, wrought iron, foundry iron, forge iron, steel, etc., and their melting or fusing points and other properties vary with the composition. In sponge form suitable for certain chemical and metallurgical applications it is obtained from its oxide ores by extraction of the oxygen at a temperature below the fusion point of the metal.

**Electrodeposited Iron** — A French process in use at Grenoble and Niagara Falls consists of electrolysing a concentrated solution of ferrous chloride at 75° C., using anodes of cast iron and a rotating mandrel of steel as the cathode. This gives a deposit of iron upon the steel mandrel of 99.966 per cent. purity and exceptional magnetic quality.

The Eustis process employs an insoluble anode at which oxidation of ferrous chloride takes place, and the metallic iron is deposited on the rotating cathode. The ferric chloride thus formed is led over pyrrhotite iron ore (the cheapest and most abundant in North America), by which it is reduced to the ferrous state, while at the same time iron passes into solution, and sulphur is deposited in the gangue and subsequently recovered as brimstone. The chemical changes that take place are represented by the equations :  $3\text{FeCl}_2 = \text{Fe} + 2\text{FeCl}_3$ , and  $2\text{FeCl}_3 + \text{FeS} = 3\text{FeCl}_2 + \text{S}$ , the iron removed from the solution being replaced by that taken from the ore. The metallic iron thus produced is of 99.99 per cent. purity, and finds application in making special steels, boiler tubes, transformers, telegraph wires, parts of aeroplane engines, and as a material for research work, being the purest available form. It is not, however, chemically pure, as it generally contains some small proportions of hydrogen, sulphur, silicon, phosphorus, and traces of carbon. By heating certain varieties of electrolytic iron in a vacuum for two hours at 1,500° C., gas is evolved equal to two and a half times its own volume, containing 6 per cent.  $\text{CO}_2$ , 34 per cent.  $\text{CO}$ , 49 to 51 per cent.  $\text{H}_2$ , 2 to 4 per cent. hydrocarbons, and other gases 7 per cent.

**Cast or Pig Iron** is made in blast furnaces from mixtures of iron ore with coal or coke and limestone, by which means (the contents of the furnace being maintained at bright-red heat by a blast of air) the oxygen contained in the oxides or other iron compounds is burned off by the carbon, the lime combines with the clayey part of the ore and

## PIG IRON AND IRON ORE, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country	Pig Iron Metric Tons	Iron Ore Metric Tons
Germany-Austria ..	18,400,000	13,300,000
United Kingdom ..	7,900,000	13,700,000
France .. ..	7,300,000	35,000,000
Belgium .. ..	3,100,000	200,000
Luxemburg .. ..	1,900,000	6,500,000
Czechoslovakia ..	1,300,000	1,500,000
Italy .. ..	900,000	1,000,000
Poland .. ..	900,000	900,000
Sweden .. ..	700,000	14,200,000
Hungary .. ..	400,000	300,000
Spain .. ..	400,000	2,000,000
Netherlands .. ..	300,000	—
Norway .. ..	200,000	1,200,000
Rumania .. ..	100,000	100,000
	<hr/>	
Yugoslavia .. ..		600,000
Greece .. ..		600,000
U.S.S.R. .. ..	15,000,000	26,000,000
U.S.A. .. ..	29,800,000	51,700,000
Canada .. ..	900,000	100,000
Mexico .. ..	100,000	100,000
	<hr/>	
Newfoundland ..		1,700,000
Cuba .. ..		300,000
Brazil .. ..	100,000	300,000
Chile .. ..		1,600,000
Japan .. ..	2,900,000	700,000
British India .. ..	1,700,000	2,900,000
Manchuria .. ..	700,000	
Korea .. ..	200,000	500,000
	<hr/>	
Malaya .. ..	5,500,000	1,800,000
Philippines .. ..		900,000
		<hr/>
Union of South Africa	300,000	500,000
Algeria .. ..		2,800,000
Spanish Morocco ..		1,200,000
Tunisia .. ..		800,000
Sierra Leone .. ..		700,000
Australia .. ..	900,000	2,300,000
Sum of above ..	96,400,000	188,000,000
WORLD PRODUCTION ..	96,400,000	192,300,000

forms the slag. The molten iron settles in a layer at the bottom of the furnace, the slag, which is less fusible, remaining on its top.

"Pig iron" made in this way, containing from 2 to 5 per cent. of carbon and small quantities of sulphur, phosphorus, and silicon, is used for making stoves, saucepans, iron gates, and many other articles. It is hard and brittle, and, as ordinarily made, is more readily fusible ( $1,100^{\circ}\text{C.}$ ) than wrought iron, which is made from it by remelting and exposure to further oxidation to burn off more carbon and other impurities. Its uses are limited for temperatures not above  $200^{\circ}\text{C.}$  (say), for low pressures, and for pressures up to 80 pounds per square inch (say) when the temperature is low (Hinchley).

In the "Bassett" process for the production of iron, the oxide is mixed with powdered coal and heated in a rotary furnace at  $1,000^{\circ}\text{C.}$  by means of powdered coal flame, the lower end of the kiln receiving the molten iron and slag. (See *Ores and their Treatment.*)

In the "Borcoud" process (which, like the "Bassett" process, is of French origin) the iron ore is similarly reduced by carbon monoxide (produced by heating pulverized coal with heated air) in a rotary furnace so lined that the gases are made to follow a long spiral path, and thus come into prolonged contact with the ore, which is made to travel in the opposite direction. In this way the sulphur and phosphorus compound constituents of the ore are not reduced at all, and the temperature of the reduction is so low that these impurities pass directly into the slag together with the silica and manganese compounds, leaving the mass of mainly pure reduced iron in the furnace ready for remelting in an electric furnace in the absence of air.

Iron is known to exist in two forms according to its temperature: the high-temperature form dissolves carbon, the low one does not. Ordinary foundry iron contains phosphorus and sulphur in the form of phosphide and sulphide, and as these melt at  $1,740^{\circ}\text{F.}$ , cast-iron fire-bars become porous by these compounds running out, leaving metal, which oxidizes rapidly at  $1,830^{\circ}\text{F.}$ , thus causing the "burning" of fire-bars, for example. A cast iron alloy named "Usco" has, it is stated, a higher melting-point, greater tensile strength than the ordinary product, and although more costly initially, can be used beneficially for many applications. (See *The Metallurgy of Iron and Steel*, by Bradley Stoughton (McGraw-Hill Book Co., New York); *Blast Furnace Practice*, by Ralph H. Sweetser (McGraw-Hill Book Co., New York).)

**Wrought Iron** (m.p.,  $1,600^{\circ}\text{C.}$ ), when heated to redness, is soft, and can be hammered and joined (welded) into any desired shape, a property which is utilized in smithcraft.

**Steel** (m.p., about  $1,350^{\circ}$  to  $1,375^{\circ}\text{C.}$ ) is produced from wrought iron, which is practically devoid of carbon, by the incorporation of carbon to the extent of from 0.7 to 1.7 per cent., but generally from cast iron by removing the excess of that impurity. It is, in practice, produced by either blowing or otherwise exposing molten pig iron to a blast of air, which burns out the carbon, together with other impurities, including silicon, manganese, and sulphur.

Steel is regarded as a definite crystalline structure in which the size, chemical composition, and disposition of the crystals are regulated by the content of carbon, the work under the hammer and rolls, and the heat treatment. Microscopic studies on polished and etched specimens have contributed largely to the understanding of the effects of chemical composition, and of heat and mechanical treatments.

The manufacture of a ton of steel from hematite ore is stated to require 3 to 4 tons coal, 2 tons of ore, and 8 to 9 cwt. limestone.

Official estimates of 1949 *capacity* for steel ingots and castings in Europe and the United States are as follows :

Country	Millions of Net Tons
U.S.S.R. .. .. .	25.0
United Kingdom .. .. .	17.5
France.. .. .	10.5
Western Germany .. .. .	10.5
Belgium .. .. .	4.5
Luxemburg .. .. .	2.6
Italy .. .. .	2.3
Saar .. .. .	1.7
Sweden .. .. .	1.3
Austria .. .. .	0.9
Spain .. .. .	0.7
Eastern Germany .. .. .	0.4
Netherlands .. .. .	0.1
Turkey .. .. .	0.1
Other European Countries .. .. .	6.6
	<hr/>
	84.7
	(1945 production 21.0)
United States of America .. .. .	99.4
	(1945 production 90.0)

France, Sweden, and U.S.S.R. have iron ore in quantity and quality to justify sizeable steel-making, but France and Sweden lack coal.

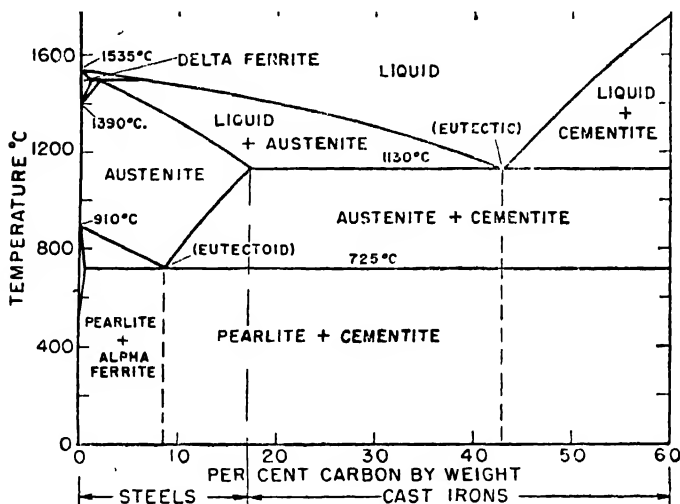
Stated *production* in 1914 was for Germany 15.2 millions of net tons of steel, for United Kingdom 8.8, for Russia 5.2, for U.S.A. 26.3, and for the World 66.6.

So-called mild steel contains from 0.1 up to about 0.4 per cent. of carbon, hardening being effected by the addition of carbon to the outer layers ; the harder varieties contain up to about 2 per cent., while the largest amount of carbon that iron can combine with is 6.67 per cent., corresponding to the formula  $\text{Fe}_3\text{C}$ .

It is the phosphorus content of the cast or pig iron that determines to some extent the particular process to be adopted for making steel therefrom. Thomas's invention, worked out in association with Gilchrist, enabled steel manufacturers to utilize great deposits of iron ore of a relatively high phosphoric character and therefore not previously suitable, and this process of dephosphorization has been so developed

that the greater bulk of steel now produced in the world is made by the so-called "Thomas-Gilchrist" process. In this, dolomite "over-burned" at a very high temperature (by which it becomes very hard and dense) is subsequently ground and mixed with boiled tar as a binder; this mixture being utilized to make the lining of the converters in which the phosphoric iron is converted into steel by burning out the phosphorus, carbon and other impurities; the phosphorus going to the slag, which thus becomes available as a valuable fertilizing agent. (See Iron (Slag).) In the absence of phosphorus to any considerable extent, the old Bessemer process suffices, in which the "ganister"

THE IRON—CARBON SYSTEM  
TEMPERATURE—CONCENTRATION RELATIONSHIPS



Austenite : Solution of carbon or cementite in gamma iron.

Delta Ferrite : Solution of carbon in delta iron.

Alpha Ferrite : Solid solution of carbon or cementite in alpha iron.

Cementite : Iron carbide,  $\text{Fe}_3\text{C}$ , containing 6.67 per cent. C.

Pearlite : A lamellar aggregate of ferrite and carbide resulting from the eutectoid reaction.

(siliceous) lining of the converter is employed, air being blown through the molten mass, thus getting rid of the carbon, but leaving some phosphorus and sulphur in the molten metal, which is made more or less brittle in consequence. The basic lining removes these impurities, as already explained.

In the so-called basic Bessemer process, in which melted pig iron is subjected to a blast of air, the lining of the converter or oxidizer is made of bricks of magnesian limestone cemented together, instead of the siliceous acid material named *ganister*, which was used in the old Bessemer process, with the result that the phosphorus is removed in addition to the other associated impurities, and concentrated in the slag.

The success of this process has depended upon the skill of the operator to judge the proper moment at which the blast was to be discontinued. The photocell has been developed so that it can supersede the human eye (see H. K. Work in *Trans. Amer. Soc. Mech. Engrs.*, **145**, 132 (1944); H. W. Graham in *Trans. Amer. Soc. Mech. Engrs.*, **145**, 113 (1941); and H. T. Bowman in *Trans. Amer. Soc. Mech. Engrs.*, **150**, 113 (1942)).

In the Siemens-Martin process of steel-making, the cast iron is mixed with specially picked iron ore, using furnaces with open hearths heated by producer gas, and the elimination of phosphorus by burning out is largely due to the high ferrous oxide content of the slag. Wide attention has been given to the use of oxygen in steelmaking to decrease the fuel consumption and to reduce the carbon content of the steel. Preliminary reports indicate that open-hearth production may be increased between 20 and 40 per cent. under this technique. Some consideration has also been given in extending its uses to the blast-furnace and Bessemer processes. (See W. A. Lloyd, *Iron Age*, **158**, 105 (Nov. 21, 1946); E. S. Kopecki, *Iron Age*, **158**, 47 (Nov. 28, 1946); G. V. Slottman and F. G. Kerry, *Steel*, Dec. 2, 1946, 106, and *Iron Age*, **159**, 109 (June 12, 1947); **159**, 75 (June 19, 1947).)

About 70 per cent. of the steel produced in the United Kingdom is made by the open-hearth process, and in the United States this percentage is over 90.

In the final casting of steel into ingots, a small quantity of aluminium is usually introduced, with the object of preventing the formation of blow-holes.

In the manufacture of steel for industrial employment, many other metals are deliberately introduced, manganese, for instance, being used for hardening purposes up to about 1 per cent. in the so-called Bessemer and open-hearth steels, although for some purposes larger quantities are used, the so-called manganese steel containing from 11 to 14 per cent. manganese, possessing certain valuable physical qualities. Nickel is used to produce a toughening effect, and chromium, cobalt, tungsten, molybdenum, tantalum, vanadium, and zirconium are severally employed to give particular properties or qualities to steels destined for special applications. The hardenability of a steel can be predicted (M. A. Grossman, *Trans. Amer. Soc. Mech. Engrs.*, **150**, 227 (1942)) from its chemical composition. The effect of individual alloying elements is shown to be independent of other elements present. A series of papers on this subject appeared in *Trans. Amer. Soc. Mech. Engrs.*, **156** (1944). It is thus possible to develop steels with desired hardenabilities through efficient and economical use of alloying elements.

Zirconium steel is extraordinarily hard, and plates of zirconium-nickel steel are stated to be twice as resistant to shot as those of chromium steel. Steel containing 12 to 14 per cent. chromium and a low percentage of carbon (about 0.3 per cent.)—**stainless steel**—has been rendered possible only by the electric furnace, which is necessary for the preparation of the ferrochrome, as also for the steel melting. Steel of this quality is passive to nitric acid of sp. gr. 1.20.

So-called "Austenitic steels" of **acid-resisting** quality are described

as consisting of a solid solution of carbides in a solid solution matrix of chromium and nickel in iron. Some of these contain up to 12 per cent. nickel, 20 per cent. chromium, and varying amounts of other special elements such as copper, molybdenum, tungsten, etc. Certain varieties of these new stainless steels are now used in high pressure apparatus for chemical plants, in making culinary utensils and other domestic articles, also in constructional work, as they take a high polish after washing with soap and water and then present a platinum or silver-like appearance.

The **hardening** of steel is brought about by rapid cooling after being heated to a high temperature, whilst the **tempering** of steel is effected by reheating the hardened metal to a temperature much lower than that used for hardening it, and cooling slowly. In special cases a modified heat treatment is used, such as directly quenching in a bath, preheated to some ageing temperature, and maintained for some duration of time before air cooling. This treatment, called *austempering*, results in a tougher product with the desired hardness than obtained by the conventional hardening and tempering operation and minimizes cracking and internal stresses. A knowledge of the sub-critical isothermal behaviour of austenite in a given steel as shown by S-curves is necessary in order to control austempering properly. See E. S. Davenport, *Trans. Amer. Soc. Metals*, **27**, 837 (1939), and references under Physical Metallurgy. Martempering is a heat treatment developed by B. F. Shepherd (*Metal Progress*, **46**, 308 (1944)) which conditions the martensite in the steel so as to reduce internal stress and distortion and still obtain a high hardness value. (See Martempering.) The nitrogenization process for hardening steels, discovered by Fry, consists of heating them in an atmosphere of ammonia, those containing about 1 per cent. aluminium responding well to this treatment and finding large employment. M. L. Guillet described a process for hardening steel, which consists of heating it in a current of ammonia at 500° to 510° C., thus producing an extremely hard layer which may amount after some time to 0.8 mm. thick, but the steel must contain certain elements which prevent penetration of the nitrogen, which otherwise produces iron nitride and makes the metal fragile.

**Ferro-Alloys** are used in the steel industry to remove oxygen and nitrogen from molten steel, or to introduce into the steel a small proportion of some other metal in order to adapt it to special applications.

To remove oxygen, from 0.5 to 1 per cent. of ferro-manganese, ferro-silicon (containing 30 per cent. or more silicon), ferro-aluminium, and ferro-titanium are variously used in very small proportions, the manganese compound being most generally used by reason of its cheapness.

To remove nitrogen, ferro-vanadium (containing from 25 to 40 per cent. vanadium) and ferro-titanium are employed; whilst to introduce the proportion of special metal, ferro-manganese, ferro-vanadium, ferro-chromium, ferro-tungsten, ferro-molybdenum, ferro-titanium, ferro-uranium, ferro-boron, and ferro-zirconium are all used.

A steel containing 12 to 14 per cent. manganese is very tough and hard, and specially adapted for mining and grinding machinery and

making burglar-proof vaults ; one containing from 2 to 4 per cent. chromium is a very hard tool-making material ; that containing 15 to 25 per cent. tungsten is a high-speed steel which will cut iron while red-hot ; that containing 6 to 10 per cent. molybdenum is similar to the tungsten variety, and is also used for lining large guns to increase their resistance to erosion. Steel containing from 0.5 to 1 per cent. vanadium is very strong, resists shock well, and is used for making motor-car axles, cranks, piston-rods, etc. The titanium combination containing from 1 to 2 per cent. of that metal is largely used for making steel rails and sheet-steel. Steel containing about 0.5 per cent. of uranium is said to replace that containing several per cent. of tungsten, and is used for making tools ; while the zirconium variety is well adapted for bullet-proof sheets, armour-plate, and armour-piercing projectiles.

**Ferro-Carbon-Titanium** is an alloy containing carbon, which is sometimes used to make steel tougher and ensure very sound castings.

**Ferro-Cerium (Pyrophoric Alloys)** — Alloys made with a mixture of rare-earth metals (chiefly cerium) with about 30 per cent. iron ; a sparking substance used in making cigar-lighters and for tracing the flight of shells, the friction of the air generating sufficient heat to cause a piece of the alloy attached thereto to burst into flame and thereby indicate their path. The cerium is obtained from the residues of the gas-mantle industry.

**Ferro-Chrome** contains from 50 to 60 per cent. of chromium and 5 to 9 per cent. of carbon.

**Ferro-Manganese** is an alloy of manganese carbide with iron, and contains from 20 to 85 per cent. of manganese.

**Ferro-Molybdenum, Ferro-Nickel, and Ferro-Phosphorus** all have their special applications in steel-making of various qualities, the latter being used when very thin castings have to be made by increasing the fluidity of the metal. (See Molybdenum.) Molybdenum does not function as a deoxidizer, and its value in steel-making is attributed to the formation of a true alloy.

**Ferro-Silicon** — Iron alloyed with from 12 to 16 per cent. of silicon is very resistant to the action of acids, and the use of this alloy has largely replaced that of glass and stoneware in chemical industry. It is somewhat brittle, and vessels made of it will not withstand great internal pressure, but up to 50 pounds per square inch they are considered safe. Another extensively used ferro-alloy is one of silicon and iron, containing 30 per cent. or more silicon, but no carbon. It is made by the reduction of silica (preferably a pure grade of quartzite) and iron ore with carbon in the electric furnace, and is used not only in making hydrogen, but also in conjunction with ferro-manganese as a deoxidizing agent for converting white cast iron into grey iron, and in steel manufacturing.

**Ferro-Vanadium** — See Vanadium.

See *Ferrous Metals*, by Birkett and Dorman (E. Benn, London) ; *Practical Steel-making*, by W. Lister (Chapman and Hall, London) ; *Acid-Resisting Metals*, by S. J. Tungay (E. Benn, London) ; Corrosion, and Rustless Iron.

**Slag (Basic Slag)**, or the cinder from blast-furnaces, consists largely of silicates of calcium and aluminium, containing also phosphates in varying proportion. When reduced to powder, it is used as a phosphatic fertilizing material; and in a crushed and pulverized state as a road-making material which, when penetrated with tar, constitutes the material known as "Tarmac." It is also used in making "Vinculum" concrete and a certain quality of glass can be made from it (see C. D. Abell on "Blast Furnace Slags" (*Ind. Chem.*, 8, 110 (1932))).

The phosphide of iron ( $\text{Fe}_2\text{P}$ ) representing the state of combination in which the phosphorus exists in molten iron is oxidized to phosphate, possibly ferrous phosphate ( $\text{Fe}_3(\text{PO}_4)_2$ ) being formed, but this substance is unstable in the presence of a large excess of iron and is itself reduced to a phosphide of iron. In the basic process, the presence of lime causes the formation of calcium phosphate. The calcium phosphate thus formed is only feebly attacked by the metallic iron, but manganese and carbon act more vigorously and cause the phosphate to be reduced and the metal to be rephosphorized, a tendency which is restrained, however, by maintaining a certain concentration of ferrous oxide.

Slag is also variously used in cement-making, as a packing material, in making fire-proof compositions and heat-insulating materials, and in powdered form in France as an insecticide for the eradication of a particular parasite affecting the sugar-beet.

A standard suggested by the British Chemical Standards Movement for basic slag "A" is as follows:

Phosphoric anhydride ( $\text{P}_2\text{O}_5$ )	..	..	12.93	per cent.
Equal to phosphates ( $\text{Ca}_3(\text{PO}_4)_2$ )	..	..	28.24	"
Iron	..	..	8.97	"
Silica	..	..	16.15	"

So-called "**slag-wool**" (slag bestos) is made from slag by blowing air or steam through or against it when in melted form, being thereby converted into fine threads like cotton-wool, and in this form it is used as an insulating material, a filtering medium, covering for steam-pipes, boilers, etc., and as a packing material. Its heat insulating power largely depends upon the fineness of its fibres. A similar product is also manufactured from rocks of appropriate character, such as natural siliceous limestone or calcareous shale, which, when in a molten state and blown by high-pressure steam, give the longest, finest, strongest, and most resilient fibres.

**Iron Carbide** — See Carbides.

**Iron Carbonyls** — See Metallic Carbonyls.

**Iron Oxides** — The three known oxides of iron are ferrous oxide ( $\text{FeO}$ ), ferric oxide ( $\text{Fe}_2\text{O}_3$ ), and the so-called magnetic oxide ( $\text{Fe}_3\text{O}_4$ , or  $\text{FeO}.\text{Fe}_2\text{O}_3$ ), the ferrous and ferric salts being derived from the first two named oxides, respectively, by combination with acids.

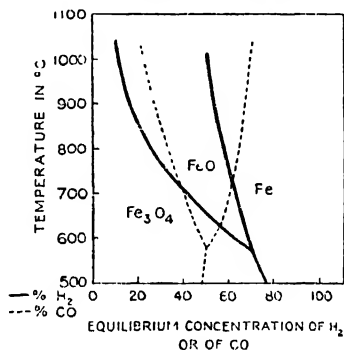
The yellow "ferrite" oxides of iron are valuable as paint pigments.

**Ferrous Oxide** ( $\text{FeO}$ ) is a black powder which oxidizes in the air. It can be made by heating ferrous oxalate in the absence of air. In

combination with water as **ferrous hydroxide** ( $\text{Fe}(\text{OH})_2$ ), it is precipitated in almost white form when sodium, ammonium, or potassium hydroxide solution is added to a solution of a ferrous salt, but it rapidly absorbs oxygen from the air, and gradually passes into ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ), which after heating is used as a pigment. This hydroxide can also be prepared in gel form. (See Colloid Chemistry.)

**Ferric Oxide** can be prepared in two interconvertible forms, magnetic and non-magnetic, and many hydrates are known to exist. The ordinary oxide (colcothar) is red and non-magnetic, while the other variety is brownish-yellow and nearly as magnetic as magnetite ( $\text{Fe}_3\text{O}_4$ ). The red variety is reduced by hydrogen at  $500^\circ\text{C}$ . to  $\text{Fe}_3\text{O}_4$ .

#### $\text{Fe}_3\text{O}_4$ AND $\text{FeO}$ AND $\text{Fe}$ EQUILIBRIUM WITH $\text{H}_2$ OR WITH $\text{CO}$



100—per cent. of  $\text{H}_2$  = per cent. of  $\text{H}_2\text{O}$  vapour.  
 100—per cent. of  $\text{CO}$  = per cent. of  $\text{CO}_2$ .

$\text{Fe}_2\text{O}_3$  is stable against  $\text{Fe}_3\text{O}_4$  at about 1 part per million of  $\text{H}_2$  or  $\text{CO}$ .

Ferrous sulphate when calcined at from  $600^\circ$  to  $1,000^\circ\text{C}$ . yields ferric oxide (red oxide) ( $\text{Fe}_2\text{O}_3$ ), the colour of the product varying considerably according to the temperature used, the lower temperatures yielding the lighter shades. There is a process (Neill's) for making it from spent pickling liquors, the ferrous sulphate prepared therefrom being roasted in a current of air to make the ferric oxide.

Rust consists of a mixture of the two hydrated oxides and ferrous carbonate, and continued exposure to air effects the oxidation of the ferrous compounds into ferric oxide ( $\text{Fe}_2\text{O}_3$ ).

Ferric oxide, by reason of its hardness, is greatly used as an abrasive and polishing material, while *bloodstone* (a hard kind of red hematite), when well polished, is considered the best material for producing a high lustre on coat buttons and on the gilding of porcelain. In the pulverulent form, the ferric oxide, obtained by the combustion of ferrous oxalate and other methods, is particularly esteemed for its grinding and polishing characters. *Jewellers' rouge* for polishing gold and silver is produced by lightly calcining ferrous sulphate, while the article named "*crocus*," used for polishing brass and steel, is produced by

**IRON CARBONYL** — See Metallic Carbonyls.

**IRON LIQUOR** — See Iron (Ferrous Acetate).

**IRON MORDANT** — Trade name for ferrous sulphate.

**IRON PYRITE** — Iron disulphide. (See Iron, and Pyrite.)

**"IRONAC"** — A proprietary, hard, cast-iron silicon alloy of acid-resisting character, advocated for use in making chemical plant. (See Iron (Ferro-Silicon).)

**IRONE** ( $C_{14}H_{22}O$ ) — A methyl ketone, formerly thought to be isomeric with ionone ( $C_{13}H_{20}O$ ), but since 1941 believed, through the work of Ruzicka, to contain an extra methyl group, as shown.

It is the odoriferous constituent of the root of the iris and of the flowers of the violet. It has not yet been synthesized, and on account of its cost, the synthetic substitutes, the ionones, are usually employed when violet essences are required in perfumery.

**IRONSTONE** — See Iron.

**IRRIGATION** — An irrigation process is often employed for the disposal of sewage, and consists in allowing it or the effluent from it (resulting from preliminary treatment or deposition of the heavier solid parts) to slowly drain off or filter through the land, over which it should be fairly evenly distributed. A light loamy soil is the most suitable, and great purification is effected, whilst the land is, at the same time, fertilized for the growth of cereals and vegetables. The nature of the purification that occurs is discussed under the heading of Nitrification. As supplies of suitable land are not generally available, specially prepared bacterial filter-beds of ashes or charcoal and other materials are generally used. (See Nitrification, and Sewage.)

**IRVINGIA** — See Dika Butter.

**ISATIN** (*o*-Aminophenylglyoxylic Acid Lactam) ( $C_6H_4.CO.CO.NH$ ) — A

synthetic, reddish-yellow, crystalline substance of m.p.  $200^{\circ}C$ ., fairly soluble in hot water, ether, and alcohol, which can be prepared by the oxidation of indoxyl ( $C_6H_4.C(OH):CH.NH$ ) with nitric acid or hypo-

chlorous acid. It is convertible into aniline by fusion with alkali at  $200^{\circ}C$ . On treatment with aqueous alkalis, the first-formed red metallic derivative is rapidly converted upon warming to the nearly colourless salt of isatic acid ( $NH_2.C_6H_4.CO.COOH$ ), due to the opening of the lactam ring. It is used in the preparation of dyes, and of certain acridine and quinoline derivatives.

**ISINGLASS** (*Ichthyocoll*) — The dried inner membranes of the swimming bladder of the sturgeon, *Acipenser huso* and other species of *Acipenser*, which are found in the Caspian and Black Seas. After removal, the bladders are cut open and soaked in water; they are then spread out and the outer silvery membranes removed by rubbing. The isinglass is then dried and marketed in sheets, known as "leaf isinglass," or in sheets folded together, known as "book isinglass," or rolled and folded in the form of a horse-shoe, known as "staple isinglass." It contains about 80 per cent. of collagen and is used as an adhesive and for clarifying wines, beer, vinegar, and pharmaceutical preparations. Inferior varieties are obtained from the bladders of cod, ling, and hake, and from sole skins, and fish-bones. (See Adhesives, Gelatine, and Glue.)

**ISO** — A prefix signifying equal or identical, as isomeric, isobares, isotopes, isomers, etc. (See Chains.)

**ISOBARS** (*Isobares*) — A term given to atoms stated to have identical atomic weights, but differing in chemical properties—a deduction made from mass-spectra observations. Two atoms of the same mass number but with different atomic numbers, for example, neptunium 239 mass number and 93 atomic number ( ${}_{93}\text{Np}^{239}$ ) and plutonium 239 mass number and 94 atomic number ( ${}_{94}\text{Pu}^{239}$ ). Radium B, radium C, and radium C' are isobaric, the atomic weight of each being 214, whereas their atomic numbers and chemical properties differ. (See Atoms, Isotopes, and Transmutation.)

**ISOCYCLIC** — See Homocyclic.

**ISO-ELECTRIC POINT** — See Proteins.

**ISO-EUGENOL** — See Cloves.

**ISOMERISM** — Substances composed of the same number of the same atoms, but differing in molecular construction (architecture) and properties, are described as *isomeric*. Thus, ordinary alcohol and methyl ether have the same percentage composition and empirical formula ( $\text{C}_2\text{H}_6\text{O}$ ), but are perfectly distinct substances, the constitutional formulas being regarded as respectively  $\text{C}_2\text{H}_5\text{OH}$  and  $(\text{CH}_3)_2\text{O}$ . There are many such cases, particularly among organic compounds, as, *e.g.*, the bodies known as terpenes—that is, the hydrocarbons forming the chief constituents of the various essential oils—all of which have the common composition  $\text{C}_{10}\text{H}_{16}$ , and yet differ largely in their chemical and physical properties. Varying amounts of heat are consumed in the formation of any two isomeric bodies, and so, when decomposed, there is a corresponding difference in the evolution of heat, showing that varying amounts of energy are required to build up the different molecular structures of isomeric bodies.

Isomers of the same molecular weight are described as metameric, while those of dissimilar molecular weights are described as polymers.

The possible number of structural isomers of the paraffin hydrocarbons is stated as follows :

Number of Carbon Atoms in Molecule	Number of Isomers
4	2
5	3
6	5
7	9
8	18
9	35
10	75
11	159
12	355
14	1,858
16	10,359

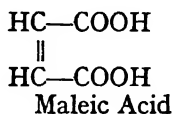
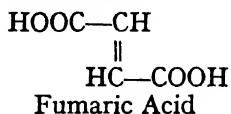
An interesting set of observations related to structural isomerism is that of G. M. Good, H. H. Vogel, and B. S. Greenfield, in *Ind. Eng. Chem.*, 39, 1032 (1947), on the effect that cracking plays *under a given set of conditions*. It is found that :

C-Structure of $C_6H_{14}$ -Hydrocarbon	Cracking Extent in Weight per cent.
$C-C-C-C-C-C$	14
$  \begin{array}{c}  C-C-C-C-C \\    \\  C  \end{array}  $	25
$  \begin{array}{c}  C-C-C-C-C \\    \\  C  \end{array}  $	25
$  \begin{array}{c}  C-C-C-C \\    \quad   \\  C \quad C  \end{array}  $	32
$  \begin{array}{c}  C \\    \\  C-C-C-C \\    \\  C  \end{array}  $	10

*Reference: Isomerism and Isomerization of Organic Compounds*, by E. D. Bergmann (Interscience Publishers, New York).

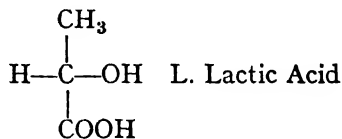
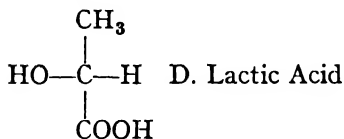
**Stereoisomerism** — This phenomenon, unlike that of the structural isomerism described above, results from the different spatial arrangements of the groups in a pair of structurally identical molecules. There are two types of stereoisomerism, geometrical and optical.

In the former, two parts of the molecule are united by a double bond and the inability of the groups concerned to rotate about such a union means that the groupings can be fixed in one of two ways relative to one another, as in the case of the geometrical isomers, fumaric and maleic acid—



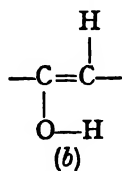
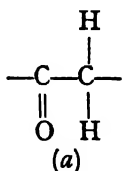
The former is known as the *trans* form and the latter as the *cis* form and it will be readily seen that the two are not interconvertible except by rupture of the double bond. Whenever a double bond occurs in a molecule geometrical isomerism is possible providing that neither of the two carbon atoms forming the double bond is connected to identical groups. Such latter compounds are not optically active as a plane of symmetry normally exists in the molecule.

Optical isomerism is exhibited by two structurally similar bodies when their molecules contain a carbon atom, the four valencies of which are each connected to a different atom or grouping, for instance the two lactic acids, one of which is called "lævo" (L, l or -), and the other "dextro" (D, d or +). The former rotates the plane of rotation of polarized light to the left and the latter to the right. An optical isomer possesses no plane or centre of symmetry, and may be said to be related to its "enantiomorph" as a left-handed glove is related to the right-handed one of the same pair.



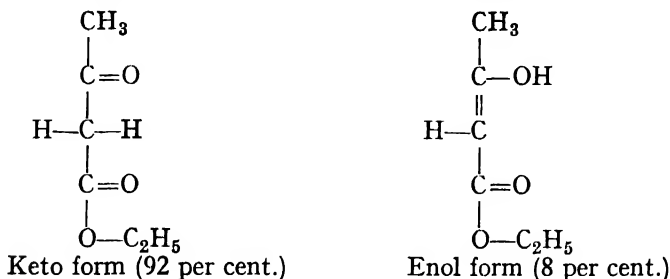
**Tautomerism** is a type of isomerism attributable to intramolecular rearrangements, so that a substance may react in accordance with varying structural formulas, and it has been suggested that the term should apply to all reversible isomeric changes.

An example of such reversible changes is afforded by certain ketonic esters, where the group (a) easily changes into the group (b), and *vice versa*.



The resultant isomers exhibit varying chemical functions, and others similar chemical properties, etc., but all are due to the particular character of the structure of the substances concerned. A classical

example of tautomerism is ethyl acetoacetate, in which there is an equilibrium between *keto* and *enol* forms at ordinary temperature, thus,



Any reagent that reacts with one of these forms (and not with the other) reacts in time with all of the ester through displacement of the equilibrium.

For detailed information concerning the various types of isomerism, such as *cis-trans*, chain, dynamic, geometrical, ionic, etc., see *Fundamental Principles of Organic Chemistry*, by Charles Moureu, translated by W. T. K. Braunholtz (Harcourt Brace and Co., New York), and *A Textbook of Organic Chemistry*, by John Read (G. Bell and Sons, London). (See Co-ordination, Formulas, Metamerism, and Polymerism.)

#### ISOMORPHISM — See Crystals.

**ISOPRENE** ( $\text{C}_5\text{H}_8$  or  $\text{CH}_2 : \text{C}(\text{CH}_3) . \text{CH} : \text{CH}_2$ ) — A volatile liquid hemiterpene, yielded by the destructive distillation of pure rubber, also obtainable from turpentine by the action of heat, and which by contact with certain reagents, such as hydrochloric acid, becomes converted partly into rubber. It is colourless, boils at  $37^\circ \text{C}.$ , and is of interest in connection with attempted syntheses of rubber on a commercial scale. (See Rubber.)

**ISOPROPYL ALCOHOL (Isopropanol, 2-Propanol)** ( $\text{CH}_3 . \text{CH}(\text{OH}) . \text{CH}_3$ ) — A secondary alcohol which yields a ketone (acetone) upon oxidation. It is a colourless mobile fluid of sp. gr. 0.786 and b.p.  $82.3^\circ \text{C}.$ , made from acetone by reduction with sodium amalgam or by catalytic hydrogenation, or by reaction of sulphuric acid with propylene of petroleum gases and subsequent hydrolysis. It is soluble in alcohol and ether and is miscible with water in all proportions; used commercially as a solvent and preservative (being as good as ethyl alcohol for the extraction of drugs like belladonna, benzoin, capsicum, cinchona, henbane, and nux-vomica), and as a solvent in making perfumes, cosmetics, etc. "Avantine" is a make of isopropyl alcohol of which 95 per cent. is of b.p.  $81^\circ$  to  $82^\circ \text{C}.$  (See Smoley *et al.* in *World Petroleum*, 18, No. 12, 78 (1947).) Isopropyl alcohol and water form an azeotropic mixture, 88 weight per cent. of alcohol, 12 of water, having boiling point at 1 atmosphere pressure of  $80.4^\circ \text{C}.$

**ISOPROPYL ETHER** ( $((\text{CH}_3)_2\text{CH})_2\text{O}$ ) — A colourless liquid of sp. gr. 0.726 and b.p.  $67.5^\circ \text{C}.$  It is soluble in alcohol and ether but not appreciably

in water (0·2 per cent.). Suggested as a blending agent with tetraethyl lead in motor fuel. It is stated that an antiknock rating of 100 can be obtained when 40 per cent. is blended with ordinary aviation gasoline. A saving of fuel of 15 per cent. and a gain in power of 30 per cent. is claimed.

**ISOTONIC** — See Osmosis.

**ISOTOPES** (See **Frontispiece for data**) — Atoms of an element having the same chemical properties but different masses. For example, chlorine is a mixture of two isotopes of atomic masses 35 and 37, made up of 17 protons plus 18 neutrons ( $\text{Cl}^{35}$ ) and of 17 protons plus 20 neutrons ( $\text{Cl}^{37}$ ). (See Nuclear Chemistry.)

**ISOVALERIC ALDEHYDE** (**Isovaleral**)  $((\text{CH}_3)_2\text{CHCH}_2\text{CHO})$  — A colourless liquid of apple odour, b.p.  $92\cdot5^\circ\text{C}$ ., sp. gr. 0·803, soluble in alcohol and ether; made by oxidation of amyl acetate, and used in perfumery and for flavouring, etc.

**IVORY** — Essentially *dentine*, the main constituent of all teeth, and chiefly obtained from the upper incisor teeth of the African elephant; containing about 57 to 60 per cent. calcium salts (chiefly phosphate), 40 to 43 per cent. organic matrix, and 0·24 to 0·34 per cent. fat. The teeth of the walrus, hippopotamus, sperm-whale, etc., furnish material which owing to its density can be used in place of ivory for many purposes.

**IVORY BLACK** — A fine, velvety, carbonaceous black, largely composed of mineral matter (65 to 75 per cent.), including calcium phosphate, prepared by carbonizing ivory-turnings and waste, and used by copper-plate printers in making their ink; also as a decolourizing and filtering agent.

**IVORY (VEGETABLE)** — See Vegetable Ivory.

“**IZAL**” — A proprietary fluid disinfectant, being a ready-prepared emulsion of phenoloids, including xlenols.

**JABORANDI** (**Pilocarpus**) — The dried leaflets of *Pilocarpus microphyllus*, a shrub indigenous to Brazil. It contains up to 0·5 per cent. of pilocarpine, together with *isopilocarpine* and *pilosine*. Preparations of jaborandi are occasionally used as hair lotions owing to its supposed effect in promoting the growth of hair. (See *Pilocarpine*.)

**JADE** (**Tremolite**) — Several distinct minerals are known by this name, the true jade, *nephrite* (a hard, tough variety of amphibole), being an anhydrous double silicate of calcium and magnesium  $(3\text{MgO}, \text{SiO}_2 + \text{CaO}, \text{SiO}_2)$  of sp. gr. about 3. Jade is greenish-white to deep green in colour, nearly as hard as quartz, and a favourite material for making ornaments and amulets. It is extensively found in China, New Zealand, Eastern Turkestan, Siberia, and the Philippine Islands. *Jadeite*, which resembles it, is a silicate of aluminium and sodium. (See *Asbestos*.)

**JALAP** — The dried root of *Ipomœa purga* (Fam. Convolvulaceæ), which is indigenous to Mexico and is cultivated in Jamaica and India. It contains from 9 to 18 per cent. of resin, 90 per cent. of which is soluble in ether and has been known as scammonin or orizabin, the remaining 10 per cent. being convolvulin which is insoluble in ether. Jalap is a drastic purgative. (See Convolvulin, and Gums and Resins (Scammony).)

**JAPAN** — A lacquer for metallic and wooden articles, made by heating a mixture of linseed oil, litharge, and Prussian blue, thinned with turpentine or naphtha.

**JAPAN TALLOW** — See Waxes.

**JAPAN WAX** — See Waxes.

**JAPANING** — Varnishing or lacquering in which the Japanese excelled, consisting in heating the varnished articles, after application of each coat, in an oven to a high temperature. Ivory black and animé varnishes are used amongst other materials, colours being introduced as required.

**JAROSITE** — A mineral hydrated basic sulphate of iron and potassium occurring in Victoria (Australia), from which red oxide of iron and potassium sulphate are obtainable.

**JASMINE OIL** — The essential oil distilled from the flowers of *Jasminum grandiflorum* and other species of *Jasminum* (Fam. Oleaceæ), of which there are about a hundred. The oil is reddish-brown in colour and contains benzyl and linalyl acetates and linalol; sp. gr. about 0.92; opt. rot.  $+2.5^{\circ}$  to  $+3.5^{\circ}$ . It is used in perfumery and soap-making. Amyl cinnamic aldehyde has been used as a synthetic substitute for jasmine oil. (See Y. R. Naves on "The Production of Essential Oil in Jasmine Blossoms" in *Perf. and Essential Oil Rec.*, 39, 214 (1948).)

**JASPER** — A kind of quartz. (See Chalcedony, and Silica.)

**JATROPHA** — A genus of euphorbiaceous plants, the root of one of which (*Jatropha manihot*) yields tapioca. (See Tapioca.)

**JAVELLE** — See Eau de Javelle.

**JELUTONG** — The resinous material from the latex of *Apocynaceæ Dyera*, used in making chewing gum. (See Gums (Pontianic).)

**"JESSOP" STEEL** — A range of alloys containing 0.25 to 0.6 per cent. carbon, 0.4 to 0.6 per cent. manganese, 0.4 to 1.2 per cent. silicon, 1 to 6 per cent. chromium, 0.5 to 0.8 per cent. molybdenum, and in some cases 0.5 per cent. tungsten and 0.75 per cent. vanadium. These alloys have good corrosion resistance and outstanding high temperature properties.

**JET** — Supposed to be wood in an advanced state of bitumenization (lig-nite), abundant in the upper lias shale near Whitby in Yorkshire, also found in Colorado, the island of Skye, and various parts of the European continent. It is of varying hardness, sp. gr. about 1.3; used as fuel and for making ornamental articles.

**JOULE** —  $10^7$  absolute units of work (ergs) or 1 volt-coulomb; represented by the energy expended in 1 second by 1 ampère in 1 ohm. One joule = 0.2392 gram-calories, and one gram-calorie = 4.185 joules.

**JOULE (JOULE-THOMPSON) EFFECT** — When gases at high pressure are forced through a porous plug or small orifice, they become cooler, excepting hydrogen, which becomes warmer, although below  $-80^{\circ}\text{C}$ . it is also cooled. The "effect" is due to internal work overcoming molecular attraction.

**JOULE'S LAW** — See Electricity.

**JUNIPER OIL** — An essential oil distilled from the dried ripe berries of *Juniperus communis* and possibly other species of *Juniperus*. It is a colourless or pale yellow liquid having a characteristic odour and burning taste; soluble in alcohol, chloroform and benzene. English oil of juniper has a sp. gr. of 0.870 to 0.890; opt. rot.  $+1^{\circ}$  to  $-10^{\circ}$ ; ref. ind. 1.476 to 1.479 at  $20^{\circ}\text{C}$ . Hungarian oil of juniper has a sp. gr. of 0.865 to 0.895; opt. rot.  $-5^{\circ}$  to  $-15^{\circ}$ ; ref. ind. 1.479 to 1.484 at  $20^{\circ}\text{C}$ . Oil of juniper is used for flavouring gins and hollands.

**JUTE** — The phloem fibres obtained from the inner bark of *Corchorus capsularis*, *C. olitorius*, and other species of *Corchorus*, which are grown chiefly in Bengal. The fibres are obtained by soaking the stems in water ("retting") and subsequent beating and combing. Jute is manufactured in Dundee and is woven, in India, into gunny bags and cloth which are used in the Southern States of America for cotton packings. It is also used in the manufacture of carpets, cellulose, twine, and paper. An analysis of an average clean sample showed a cellulose content of 69.63 per cent. and lignin, 18.83 per cent. The affinity of jute fibres for basic dyes is discussed by P. B. Saricar *et al.* in *Sci. and Cult.*, 12, 108 (1946), and *Nature*, 157, 486 (1946); and "The Absorption of Methylene Blue by Jute Fibres" by Sakar and Chatterjee in *J. Soc. Dyers and Col.*, 64, 218 (1948).

**KACHI GRASS OIL** — The grass *Cymbopogon cæsius* gives by steam distillation 0.14 to 0.37 per cent. of oil resembling ginger-grass oil; sp. gr. 0.927 to 0.934, acid value 0.9 to 2.5, sap. v. 13.2 to 31.2. It darkens upon exposure, and is said to contain dipentene, limonene, geraniol, and perillic alcohol.

**KAFIR** — See Sorghum.

**KAINITE (Kainit)** — One of the Stassfurt mineral deposits, consisting of potassium and magnesium salts, variously represented as  $\text{K}_2\text{SO}_4$ ,  $\text{MgSO}_4$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$ , used as a fertilizer in respect of crops such as oats, and stated to kill certain undesirable weeds, including charlock. (See Potassium.)

**KALAW SEEDS**, from *Asteriastigma macrocarpa* and other species, yield a vegetable oil.

**"KALKAMMON"** — A mixture of chalk (30 per cent.) with ammonium chloride used as a fertilizer.

**"KALSOMINE"** — A preparation of china clay for colours, such as reds, greens, and blues, which are not alkali-proof.

**KAOLINS** — Forms of china clay, approximately  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , which upon dehydration at high temperatures are resolved into  $\text{Al}_2\text{SiO}_5$  or  $\text{Al}_2\text{SiO}_7$ .

For medicinal purposes, kaolin is prepared in two forms. *Light kaolin* is used for internal administration and consists of a purified native aluminium silicate free from gritty particles. The *British Pharmacopœia* (1948) prescribes tests limiting the proportion of coarse particles present and particles greater than 10 and 3 microns in diameter. *Heavy kaolin* is also free from gritty particles, but no limit on the particle size is specified; the *British Pharmacopœia* states that heavy kaolin is to be used only for the preparation of kaolin poultice. (See Clays, Porcelains, and Sillimanite.)

**KAPAYANG OILS** — Seeds of *Hodgsonia heteroclita* and *Pangium edule* yield kapayang oils to the extent of 57.4 and 21.9 per cent. respectively, having a density of 0.922, sap. v. 203.9 and 199.5, and i.v. 63.6 and 107.3.

**KAPOK** — The Malay name given to the cotton-like down produced in the seed-pods of the tree of that name (*Eriodendron anfractuosum*), and extensively used in making life-saving jackets, etc. The dried seeds yield about 22 per cent. of oil, of sp. gr. 0.9217 to 0.9235 at 15° C., i.v. of about 95, and sap. v. about 190; used as food and for soap-making. The cake contains about 4 per cent. nitrogen and is of value as a feeding stuff. (See "Analysis of Java, Sumatra, and Malaya Oils," by R. C. Malhotra (*Analyst*, 57, 785 (1932)).)

**KARAYA GUM** — See Gums and Resins.

**"KARBOS"** — A char made from charred sawdust purified by acid treatment, and admixed with animal carbon; used for decolourizing.

**"KAROLITH"** — A casein-formaldehyde plastic.

**KARRI BARK** (*Eucalyptus diversicolor*) — A source of tanning material.

**KATHAROMETER** (Shakespear) — An instrument for measuring the thermal conductivity of a mixture of gases of known nature to determine its composition.

**KAURI GUM** — See Gums and Resins.

**KAURI OIL** — Obtained by the distillation of the gum-containing peat from the kauri gum-lands of North Island (Auckland), the yield being about 40 gallons per ton. It consists largely of the products of cracking the gum which is distributed in the peat, and resembles in complexity of character crude resin oil.

**KAVA** (Kava-Kava) — The dried, peeled rhizome of *Piper methysticum* indigenous to the Sandwich Islands. It contains a resin which contains a crystalline acid substance,  $\text{C}_{13}\text{H}_{12}\text{O}_3$ , melting between 164°

and 165° C. The plant is also grown in India and the bark (Kauwa Bark), which contains about 35 per cent. of tannin and 40 per cent. of calcium oxalate, is used as a tanning material.

**KEENE'S CEMENT** — See Cement.

**KEILHAUTE** — See Thulium.

**KELP** — The ashes of burnt sea-weeds, containing sodium carbonate, sulphate and sulphide, together with the chlorides of potassium and sodium, and insoluble substances comprising calcium carbonate, silica, and alumina. Kelp was at one time utilized for the extraction of both alkali and iodine, the latter being recovered from the mother-liquor remaining after the crystallization of the salts from the extracted ashes. Two published analyses are as follows: Potassium sulphate 8.0 and 19.0 per cent.; soda as carbonate and sulphide 8.5 and 5.5 per cent.; and potassium and sodium chlorides 36.5 and 37.5 per cent.; and thus a total of 53.0 and 62.0 per cent. of soluble salts.

In one process, the dried kelp is fed into a retort kept at a temperature of about 980° C. to obtain oil, cresote, ammonia, etc., by distillation, and the charred residual mass is cooled, ground, and lixiviated, first of all with a concentrated brine, fresh water being used for the final extraction. According to King (Fuel Research Board, Tech. Paper No. 9), a ton of dry sea-weed gives about 8.18 cwt. of solid residue, 22.4 gallons tar, 48.4 gallons liquor capable of yielding 33 lbs. of ammonium sulphate, and 3,857 cubic feet of combustible gas (14.7 therms) by low-temperature distillation method, the iodides and other salts being contained in the residue. The charcoal residue contains 35.74 per cent. carbon and 64.26 per cent. ash, from which latter the potash salts and iodine (amounting to about 0.5 per cent. NaI on the dry weed) can be obtained. A ton of kelp (obtainable from 20 tons of wet weed) is said to yield 5 cwts. of potassium chloride, 2 cwts. of potassium sulphate, 3½ cwts. of kelp salt (sodium chloride), and 9½ cwts. of waste—that is, insoluble matter resulting from lixiviation.

The pressed coke can be saturated successively with hot hydrochloric acid and water, and after pulverization is used as a decolourizing agent. After removal of the sulphates from the brine liquor, it is concentrated in a vacuum pan to a certain point and then transferred to a vacuum crystallizer, in which the potassium chloride deposits. Upon further concentration the sodium chloride separates, whilst from the mother-liquor iodine is obtained.

In another process, the kelp is fed into one end of a rotary kiln, in which it encounters a flame of burning oil from the other end, thus producing a charcoal-like mass which is subsequently quenched, ground, and leached (lixiviated), or it may be burned to a grey loose ash with a potassium content equal to about 35 per cent. K<sub>2</sub>O.

About 8 pounds of iodine can be extracted from a ton of Scotch kelp. (See Barilla, Iodine, Sea-weeds, Varec, and Vriac.)

**"KENNAMETAL"** — Tungsten-titanium carbide (WTiC<sub>2</sub>), employed as a sintered carbide for the manufacturing of high-speed cutting tools and other similar items.

**KERASIN** — A nitrogenous non-phosphorized principle of brain-matter.

**KERATIN** — A fibrous protein occurring in epithelial tissue, hair, horn, feathers, and nails, and yielding, upon hydrolysis, the following amino-acids, in the proportions indicated : glycine, 1 per cent. ; alanine, 4 per cent. ; valine, 3 per cent. ; leucine and isoleucine, 12 per cent. ; cystine, 12 per cent. ; proline, 4 per cent. ; glutamic acid, 15 per cent. ; aspartic acid, 7 per cent. ; arginine, 10 per cent. ; and lysine, 3 per cent.

**KERMES** — The oldest dye on record, being the dried bodies of a female insect (*Coccus ilicis* L.), collected in Africa and some eastern parts of Europe, and used for dyeing scarlet " fez " skull-caps, but the colour, which is chemically related to carminic acid, has less bloom than that given by cochineal. It is stated to be useless as a dye without the use of a mordant. With aluminium mordant it gives a crimson colour.

**KERMESITE (Kermis)** — An antimony ore ( $2\text{Sb}_2\text{S}_3, \text{Sb}_2\text{O}_3$ ), of crystal system No. 4, and sp. gr. 4.5.

**" KEROL "** — A phenoloid disinfectant which emulsifies with water.

**KEROSENE** — A mineral illuminant and fuel oil fraction which can be distilled from the natural petroleum deposits in America, Papua, New Guinea, Australia, etc. Sp. gr. about 0.800 to 0.810 and b.p. ranging from  $150^\circ$  to  $300^\circ \text{C}$ . (See Petroleum.)

**KESSO OIL (Japanese Valerian Oil)** — A green oil of some medicinal value ; sp. gr. 0.965 to 1.000, opt. rot.  $20^\circ$  to  $35^\circ$ , and ref. ind. 1.4775 to 1.4875. (See Valerian.)

**KETO** — Prefix used in organic chemical nomenclature and signifies the substance has the characteristics of a ketone (see same).

**KETONES** — A class of organic bodies produced by the oxidation of the secondary alcohols, and characterized by containing the carbonyl group ( $>\text{C} : \text{O}$ ). They are closely related to the aldehydes, which also contain this group, but which have the further restriction that to the carbonyl group is attached one hydrogen atom, thus,  $\text{H.CO}$ . Acetone (dimethyl-

ketone) ( $\text{CH}_3.\text{CO}.\text{CH}_3$ ) is the simplest ketone, which is related to the secondary alcohol, isopropyl alcohol ( $\text{CH}_3.\text{CHOH}.\text{CH}_3$ ), and to the

aldehyde, acetaldehyde ( $\text{CH}_3.\text{C} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{H} \end{smallmatrix}$ ). Oxidation of isopropyl alcohol

yields acetone, and reduction of acetone yields isopropyl alcohol.

When the methyl groups of the formula of acetone are replaced, one by one, by alkyl or aryl groups, other ketones result. Ketones containing two  $>\text{C} : \text{O}$  groups are termed diketones.

Methylethyl ketone (methyl acetone, 2-butanone) ( $\text{CH}_3.\text{CO}.\text{C}_2\text{H}_5$ ), a so-called mixed ketone (the alkyl groups being different), is a colourless inflammable liquid of acetone-like odour with a sp. gr. of 0.805, b.p.  $79.6^\circ \text{C}$ . ; used in making smokeless powder and as a solvent.

Ketones are reactive, forming oximes, hydrazones, semicarbazones, and with Grignard reagents tertiary alcohols. (See Acetone, Acetophenone, Acetaldehyde, Acetic Acid, Benzophenone, Oximes, and Phenylhydrazine.)

**KETOSES** — Monosaccharides containing a ketone group. (See Carbohydrates, and Fructose.)

**" KHARSULPHAN "** — See Arsphenamine.

**KICK'S LAW** — See Crushing.

**KIER BOILING** — A term used in respect of boiling textile tissues with caustic soda solution with or without pressure ; or with a mixture of lime and water. Sodium carbonate is sometimes used as a milder alkaline reagent, and sometimes the term " scouring " is used to describe the operation. Unless the cotton waxes and resinous contents are well removed the subsequent bleaching is rendered more difficult.

**KIESELGUHR (Infusorial Earth, Diatomite)** — There are many grades, one of the best—a soft, white, porous, light, earthy deposit of hydrated silica—being the siliceous skeletons of minute aquatic plants known as diatoms, found at Digby Neck, Nova Scotia, Canada, in Germany, California, and many other parts of the world. It is generally associated with earthy impurities, and contains from 65 to 87 per cent.  $\text{SiO}_2$ , 2.3 to 11.7 per cent.  $\text{Al}_2\text{O}_3$ , up to 3 per cent.  $\text{Fe}_2\text{O}_3$ , small proportions of the oxides of calcium, magnesium, potassium, and sodium, and from 5 to 14 per cent. water.

It is of great absorbent capacity, one variety being capable of taking up about four times its own weight of water and having a sp. gr. of about 0.33. Calcination is often resorted to for the removal of organic matter and improvement of colour.

It is largely and variously used as an absorbent for carrying liquid petroleum ; in the manufacture of dynamite ; as a filtering material in the sugar industry ; in ceramics ; as an abrasive, cleanser, and polishing agent ; as a filler ; and in compounding mixtures for boiler coverings. (See Infusorial Earth, Silicon, and Tripoli.)

**KIESERITE** — Mineral magnesium sulphate ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ) found in the Stassfurt salt deposits, and used for making Epsom salts.

**KILNS** — See Furnaces.

**KILO (Kilogram)** — See Weights and Measures.

**KILOMETRE** — See Weights and Measures.

**KIMMERIDGE CLAY or SHALE** — The lowest series of the upper oölite found as a deposit under the sands beneath the Portland stone of Dorsetshire and elsewhere, abounding in animal and vegetable matters. It is used to some extent as fuel, and yields on distillation petroleum-like products containing a high percentage of sulphur (5 to 8 per cent.), some of it being in the form of thiophene and homologues. (See Petroleum, and Shale.)

**KINETIC THEORY** — See Gases.

**KINETICS, CHEMICAL** — See Catalysis, Chemical Interactions, and Esters.

**KING'S YELLOW** — Trade name for arsenic trisulphide.

**KINO** — The juice, evaporated to dryness, obtained from the trunk of *Pterocarpus Marsupium*, a tree cultivated in Ceylon and Southern India. The juice is obtained by making longitudinal incisions into the bark and on drying it readily breaks up into small angular fragments. It contains from 70 to 80 per cent. of kinotannic acid which, on oxidation, yields a dark red phlobaphene. Kino is used in medicine for its astringent properties.

Other varieties of kino are known in commerce. African kino, obtained from *Pterocarpus erinaceus*, is particularly rich in tannin and is used in both the tanning and textile industries. Eucalyptus kino (Red Gum) consists of the dried juice of *Eucalyptus rostrata* and other species of *Eucalyptus* growing in New South Wales. American kino is derived from *Coccoloba urifera*. (See Tannins.)

**KIPP'S APPARATUS** — See Gas Generators.

**"KIRKSITE 'A' ALLOY"** — A zinc-rich alloy containing aluminium, copper, and magnesium similar to the Zamak alloys, employed exclusively as dies for cold forming some ferrous and non-ferrous alloys because it was found to be very economical for short-run production.

**KIRSCHWASSER** — An alcoholic liqueur obtained by fermenting and distilling pulped cherries.

**KISH** — Crystalline graphite separating from molten high-carbon cast iron and floating on the surface.

**KISIDWE NUT FAT** — From a species of *Allanblackia* (probably *A. floribunda*) growing on the Gold Coast. A hard, white fat of faint odour yielded to the extent of 73·2 per cent. by extraction with light petroleum, calculated on the dry kernels, or 44·2 per cent. upon the entire nuts; fit for soap-making, but the residual meal is bitter and astringent. The shell forms 38 per cent. of the nut.

**KJELDAHL'S PROCESS** for determining the nitrogen content of ammonia-nitrogen organic substances, principally proteins, consists of heating with concentrated sulphuric acid after addition of a little anhydrous potassium sulphate (in order to raise the boiling-point), and generally a catalyst, such as copper sulphate or mercuric oxide, whereby the nitrogen content is converted into ammonium sulphate, and on rendering the mixture alkaline with sodium hydroxide the ammonia is distilled off and the amount determined. It is used, among other purposes, in respect of blood and oil-seed meals, and most organic compounds containing "ammonia-nitrogen," but is not universally applicable to organic nitrogen compounds.

**KNOCK RATINGS** — See Cetane Rating, and Octane Rating.

**KNOPPERN (Knopper Galls)** — A tannin material in the form of excrescences produced by insects (*Cynips calicis*) upon the immature acorns or flower-cups of certain species of oak (principally *Quercus cerris* of the Slavonic plains) and known as *sisarca* and *gubacs*.

**KOJIC ACID** — See Saki.

**KOKA-SEKI** — A variety of pumice found in the Niijima Islands, used as a building material and for the construction of reinforced concrete barges, etc. (See Pumice Stone.)

**KOLA (Cola Seeds, Kola Nuts, Soudan Coffee)** — The dried seed-kernels of *Cola vera* (Fam. Sterculiaceæ), a large tree cultivated in West Africa. It contains about 1.5 per cent. of caffeine together with a trace of theobromine and is used for the preparation of stimulating drink. (See P. Casparis, *B.C.A.*, A, 1930, 1223; and Rosenthaler, *Pharm. Acta Helv.*, 10, 90 (1935).)

**"KOLLAG"** — See Lubricants.

**"KONTAKT"** — A liquid saponifier for use in the Twitchell process.

**KOPP'S LAW** — The molecular heat (specific heat  $\times$  molecular weight) of a compound is equal to the sum of the atomic heats (specific heat  $\times$  atomic weight) of the elements contained in the compound. This relationship was first pointed out by J. P. Joule (1844) and subsequently by A. C. Woestyn (1848) and H. Kopp (1865).

**KÖRYŌ OIL (Millet Seed Oil)**, from *Andropogon sorghum*, var. *vulgaris*, Hack (Mancha).

**KOUMISS** — Fermented mare's milk used in Tartary as a vinous food; something similar is said to be made in the Orkneys. An intoxicating spirit called "rack" is distilled from koumiss.

**"KOVAR"** — A low-expansion alloy used for sealing metal into hard glass, and containing about 30 per cent. nickel, 15 per cent. cobalt, 0.2 per cent. manganese, and the remainder iron.

**"KRAFT"** — See Paper.

**KRAMERIA (Rhatany Root)** — The dried root of *Krameria triandra*, a shrub growing in Peru, Bolivia, and Brazil. It contains about 8 per cent. of krameriatic acid and a dark red phlobaphene (krameria red) produced by the decomposition of krameriatic acid. It is used in medicine for its astringent properties.

**"KRENITE"** (Du Pont) — Trade-mark for a dormant spray based on sodium dinitro-ortho-cresylate. Used for controlling aphids, tent caterpillars, and peach leaf curl, and as a ground spray for apple scab and cherry leaf spot.

**KRYPTON (Kr)** — Atomic weight, 83.7. See Elements for other data. Krypton is a rare element isolated from liquefied air, and contained in the air to the estimated extent of 1 part in 2,000,000. It is a colourless and inert gas; no chemical compounds of it are known.

**KUKKERSITE (Kukersite)** — See Shale.

**KUPFERNICKEL** (NiAs) — A mineral of crystal system No. 3, and sp. gr. 7·3 to 7·6. (See Nickel, and Arsenic.)

**KURRAJONG SEED OIL** — The seeds of kurrajong (*Brachychiton populenum*) yield about 17 per cent. of a clear, red, syrupy oil of semi-drying character, with a sp. gr. 0·9206, sap. v. 189·5, and i.v. 97.

**KUSUM OIL** — See Macassar Oil.

**KUTEERA** — See Gums and Resins (Bassora).

**K-VALUES** — See Equilibrium Ratios.

**KYANIZING** — A process to protect wood against decay by treatment with an aqueous solution of mercuric chloride. The wood is steeped in a  $\frac{2}{3}$  per cent. solution, kept up to strength by adding more of the salt from time to time, different species of wood exhibiting variations in rate of absorption. Fir and pine wood must be treated for ten and seven days respectively to attain equal absorption. (See Wood.)

**LABDANUM** — A perfumery base of resinous nature which collects on the fleeces of sheep from certain species of rock rose, and from which it is combed.

**LABRADORITE** (Labrodite) — A mineral of the lime-soda feldspar order, of crystal system No. 6, and sp. gr. about 2·7, which takes a beautiful polish and exhibits changing colours (iridescence).

**LAC** — See Shellac.

**LACHESINE CHLORIDE** — An amorphous white solid, being  $\beta$ -benzilyloxyethylmethylethylammonium chloride; soluble in water, and in alcohol; insoluble in ether and in chloroform; m.p. 212° to 216° C. Used as a mydriatic in place of atropine and homatropine.

**LACMOID** (Resorcinol Blue)  $\left( \text{C}_6\text{H}_3(\text{OH})\cdot\text{NOH}\cdot\text{C}_6\text{H}_3(\text{OH}) \right)$  — Lustrous,

dark-violet, crystalline scales; used as an indicator; prepared from resorcinol by treatment with sodium nitrite; soluble in alcohol, ether, but only slightly so in water. (See Volumetric Analyses.)

**LACQUERS** — Natural varnishes, as, for example, the milky latexes of certain trees; others consisting of shellac (with or without added hard gums) dissolved in alcohol or other solvent, and coloured as desired with saffron, annato, dragon's blood, etc.; also the various nitrocellulose and cellulose acetate solutions, some millions of gallons being now annually made from pyroxylin. These last-named lacquers, which are extensively used for the carriage work of motor-cars, are almost exclusively applied by spray. A great saving of time is thereby gained by their use.

The "blooming" of freshly lacquered surfaces is generally due to the use of constituent materials which allow the dew-point of the atmosphere to be too quickly reached by reason of rapid volatility, thus

causing the deposition of moisture and consequent precipitation of the body from solution. Frosting effects in certain lacquers can be produced by introducing some finely powdered synthetic resins which are initially soluble in the combined solvents, but which subsequently crystallize out upon the evaporation of the solvents.

Cellulose acetate lacquers possess advantages over nitrocellulose lacquers, being non-inflammable and exhibiting greater stability, while non-inflammable chlorinated solvents may be used in respect of them. Lacquers consist of two parts, namely, the volatile solvents used in their preparation and the non-volatile portions; the former being the nitrocellulose solvent alcohol and hydrocarbon, and the latter the nitrocellulose, the plasticizer, and any pigments used in compounding them. The proportions and other details vary according as to whether the product is to be used for films or as lacquers.

*References:* "Lacquer and the Canning Industry," by A. Samson (*Chem. and Ind.*, **51**, 95 (1932)); "Lacquer Development during 100 Years," by D. R. Wiggam and W. E. Gloor (*Ind. Eng. Chem.*, **26**, 551 (1934)); *Solvents (for Lacquers)*, by T. H. Durrans (Chapman and Hall, London); *The Cellulose Lacquers*, by S. Smith (Sir Isaac Pitman and Sons, London); *A Survey of Nitrocellulose Lacquers*, by B. K. Brown and F. M. Crawford (Reinhold Publishing Corp., New York); *Nitrocellulose Lacquer Manufacture*, by R. G. Daniels (Leonard Hill, London); and a Memorandum on the Manufacture, Use, and Storage of Cellulose Lacquers (Form 826, H.M. Stationery Office); Dopes, "Duco," Nitrocellulose, Pyroxylin, and Varnishes.

### LACTIC ACID (Alpha-Hydroxypropionic Acid) ( $\text{CH}_3\text{CHOH}\cdot\text{COOH}$ ) —

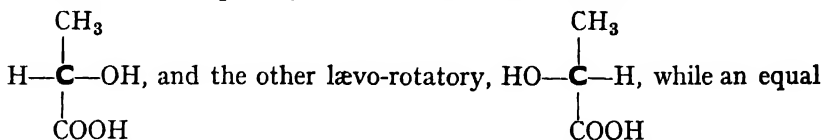
There are two isomeric varieties of lactic acid. The common lactic acid is represented as above, and that of ethylene-lactic ( $\beta$ -hydroxypropionic) acid as having the constitution  $\text{CH}_2(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . The ordinary lactic acid of commerce results from, and is largely manufactured by, the bacterial fermentation of milk, whey, cane or grape sugars, maize, and starch, using the *lactic bacilli* which cause the acidity of soured milk. As thus made from starch, milk, or sugar, the acid is neutralized as the fermentation proceeds (at a temperature of about  $34^\circ\text{C}$ .) by addition of calcium carbonate, and the solution of calcium lactate is subsequently concentrated and decomposed with sulphuric acid. When sterilized saccharine matter, such as glucose, is used in this process in the presence of chalk and nitrogenous matter, very high yields of calcium lactate are obtained. It is also produced by the action of sodium or potassium hydroxide solution upon grape or cane sugar with heat.

The pure liquid acid has a sp. gr. of about 1.249, is soluble in water and alcohol, and used in the leather and textile industries, also in medicine, mordanting, etc. It is best known in a state of solution, but can be obtained in crystalline form, which melts at  $18^\circ\text{C}$ . Lactic acid is said to be rapidly replacing the more expensive citric and tartaric acids in the compounding of soft drinks and infant foods in the U.S.A., while a small addition is stated to improve the quality of beer

K.C.E.—20

of low-alcohol content by combining with the amines and amino-acids. For commercial and edible purposes, lactic acid is prepared of 22 per cent. and 44 per cent. strengths.

There are two optically active modifications of this acid, one dextro-



part mixture of the two is of inactive or racemic character.

Upon heating, lactic acid is partially converted into lactide ( $\text{C}_6\text{H}_8\text{O}_4$ ) by the loss of 2 molecules of water from 2 molecules of lactic acid, of m.p.  $125^\circ \text{C.}$ , and when heated with dilute sulphuric acid, it splits up into acetaldehyde and formic acid. All the lactates are soluble in water.

**LACTOMETERS** (*Galactometer, Lacto-Densimeter*) — Instruments for determining the purity of milk by its specific gravity, in order to ascertain if water has been added or cream removed therefrom.

**LACTONES** — Cyclic anhydrides or cyclic esters of the gamma (1, 4) and delta (1, 5) hydroxyacid series, of which *gamma*-hydroxybutyric acid ( $\text{CH}_2\text{OH}.\text{CH}_2\text{CH}_2.\text{COOH}$ ) is an example, formed by the elimination of 1 molecule of water from a hydroxyl group and a carboxyl group present in the same molecule. Lactides are similar compounds of alpha (1, 2) hydroxyacids, one of which is described under Lactic Acid.

**LACTOSE or MILK SUGAR** ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}.\text{H}_2\text{O}$ ) — A sugar belonging to the class known as the reducing disaccharides. Chemically, lactose is 4-( $\alpha$ -glucopyranoso)- $\beta$ -galactopyranoside, being a galactoside of glucose. On hydrolysis, it is split into equimolecular amounts of glucose and galactose.

Lactose is obtained from milk, which contains about  $4\frac{1}{2}$  per cent., by concentrating and crystallizing the whey or by-product resulting from cheese-making. It is not so sweet as sucrose, is soluble in water, and used in foods, pharmacy, brewing, and medicine. (See *An Introduction to the Chemistry of Carbohydrates*, by Honeyman (Clarendon Press, Oxford).)

**LADANUM OIL** — A yellow essential oil of ambergris odour and sp. gr. 1.01, obtained by distillation of the gum resin of *Cistus creticus* and other kinds of cistus growing in Crete and parts of Asia Minor; used in perfumery.

**LÆVO-ROTATORY** — See Polarization, and Isomerism.

**LÆVULOSE** — See Fructose.

**L'AFZELIA BRIEYI** — Found in the Belgian Congo, yields an oil without preliminary decortication to the extent of 29.84 per cent. on the dried fruit; ref. ind. 1.475, sap. v. 184, and i.v. 144.

**LAKES** — The pigments obtained, as a rule, by precipitation from dyestuffs and other colouring matters. Some are formed by combination with such materials as tannic acid, casein, resin soap, and sodium phosphate, and others with some metallic hydroxide. Aluminium hydroxide ( $\text{Al}(\text{OH})_3$ ) enters into combination with many soluble organic colouring matters, thus precipitating them as so-called "lakes" in calico-printing and dyeing. The aluminium hydroxide acts as the mordant, but the same dye can give rise to different coloured lakes according to the nature of the mordant that is used. As many salts of calcium, magnesium, zinc, chromium, and tin, etc., are used, a wide range of pigments can be obtained. The lakes produced from certain dyestuffs are useless as pigments owing to their hard and horny nature, but if produced on a suitable base or "extender," such as barytes, china clay, blanc fixe, etc., this difficulty is overcome. Lakes are also used in the preparation of lithographic and printing inks. (See *The Manufacture of Lakes and Precipitated Pigments*, by A. W. C. Harrison (Leonard Hill, London) ; Dyes, Inks (Printing), and Pigments.)

**LAMBERT'S LAWS** — See Photometry.

**LAMP-BLACK** — Finely divided carbonaceous deposit resulting from the imperfect combustion of natural gas and lamp and other oils and fatty substances, naphthalene, etc. The blackening of the glass chimney of a paraffin lamp is due to the deposition of lamp-black. It is manufactured of great purity for use in making blacking, black paint, brushes for dynamos, carbons for arc-lamps and electrodes, printer's ink. (See Carbon.)

**"LAMPEN" BALL MILL** — An appliance for testing wood-pulps by beating.

**LANARKITE** (crystal system No. 5, and sp. gr. 6.3 to 7.0) — See Lead.

**LANATOCIDE C** — See Digitalis.

**"LANETTE WAX S.X."** — See Waxes.

**"LANITAL"** — A synthetic fibre made from casein, and sometimes called "synthetic wool." The casein is dispersed in alkaline solution containing carbon disulphide. Coagulation of the extruded fibre takes place in sulphuric acid. This is followed by a drying process, and subsequent treatment with formaldehyde and a plasticizer to improve the resistance of the fibre to water, to harden the fibre, and to render it elastic. "Lanital" is generally cut into short lengths and mixed with natural wool for the production of textile materials.

**LANOLINE** — See Adeps Lanæ.

**LANTHANITE** — A mineral containing lanthanum carbonate associated with cerium carbonate (crystal system No. 4, and sp. gr. 2.6).

**LANTHANUM (La) and its Compounds** — Atomic weight, 138.92. See Elements for other data. Lanthanum is a rare-earth element belonging to the cerium group of the same, found in *cerite*, *allanite*, and *lanthanite*, also in *orthite* in Greenland, and in association with other elements in

*gadolinite* (*ytterbite*). It is a metal of lead-grey colour, and can be prepared by the electrolysis of fused lanthanum chloride. It readily oxidizes in the air and decomposes water slowly with the evolution of hydrogen. As an alloying component, lanthanum forms a series of metallic compounds with such metals as aluminium, copper, gold, lead, magnesium, silver, thallium, and tin. The salts of lanthanum in solution are colourless, and upon addition of a solution of alkaline hydroxide a bulky, gelatinous hydroxide ( $\text{La}(\text{OH})_3$ ) is precipitated.

Lanthanum forms an **oxide** ( $\text{La}_2\text{O}_3$ ), insoluble in water; a **chloride** known in the anhydrous state ( $\text{LaCl}_3$ ), which is soluble in alcohol, and can also be obtained in a crystalline form ( $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ ); also a number of other compounds, including the **nitrate** ( $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), the **sulphate** ( $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ), both of which are crystalline salts soluble in water, and the **carbonate** ( $\text{La}_2(\text{CO}_3)_3 \cdot 8\text{H}_2\text{O}$ ), which is used in making incandescent gas mantles.

**LAPIS LAZULI** — A translucent, fine blue, native compound silicate of aluminium, calcium, and sodium of crystal system No. 1, and sp. gr. about 2.4, found in crystalline limestone on the Indus, and in granite in Persia, China, and Siberia. It is highly valued as a beautiful mineral for vase-making, and at one time "ultramarine" was prepared from it.

**LARD and LARD OIL** — Hog-fat has a sp. gr. 0.935, m.p. from  $41.3^\circ \text{C}$ ., sap. v. 196, ref. ind. 1.4539 at  $60^\circ \text{C}$ . The oil cold-pressed from lard has a sp. gr. of from 0.915 to 0.923, sap. v. about 195, and i.v. 56 to 74. It contains a large percentage of olein with varying percentages of the glycerides of solid fatty acids, including a little arachidonic acid. (See Brown and Deck (*J. Amer. Chem. Soc.*, **52**, 1135 (1930)); T. McLachlin (*Chem. and Ind.*, **51**, 167 (1932)); and Stillman (*J. Amer. Oil Chemists' Soc.*, **25**, 14 (1948)).) It is soluble in alcohol, ether, benzol, etc., and is variously used as food, lubricant, in soap and candle-making, for oiling wood, and in compounding metal-cutting preparations, etc. Its tendency to rancidity is lessened by slight hydrogenation, or, in the case of use in pharmacy, by the addition of small amounts of aromatic substances, such as benzoïn. (See Fats.)

**LARKSPUR** — See Delphinine.

**LATENT HEAT** — See Heat.

**LATEX** — The sap of plants, supposed in certain cases to precede the formation of cells. Rubber latex is an important article of trade. Gutta-percha is the coagulated product of latex from the *Isonarda percha* tree. (See Gutta-Percha, and Rubber.)

**LAUDANUM** — Tincture of opium, containing 1 per cent. of morphine, together with the other water-soluble constituents of the drug, in a solution of approximately 50 per cent. alcohol. It is a powerful sedative and analgesic, and possesses all the properties of opium itself. For an interesting account of its habit-forming properties, see *Confessions of an English Opium-eater*, by de Quincy, who took up to 5,000 drops a day.

**LAUGHING GAS or NITROUS OXIDE** — See Nitrogen Compounds.

**LAUREL OIL (Bay Oil)** — A bright, yellow, volatile oil of aromatic odour, soluble in alcohol, ether, and chloroform; distilled from the berries and leaves of *Laurus nobilis*, and used in medicine; sp. gr. 0.915 to 0.936 at 15° C., and opt. rot. -15° to -25°. It contains 25 to 50 per cent. cineol, together with some pinene, linalool, and eugenol, etc. It is also accompanied with a saponifiable oil containing lauric acid, obtained when the leaves or berries are boiled with water, and the laurel soap made from it is of medicinal value. The leaves yield about 2.4 per cent., and the berries about 1 per cent. oil. The berries of the Californian *Oreodaphne Californica* are stated to yield 7.6 per cent. oil. The fat extracted with light petroleum from the fruit freed from shells and purified from the accompanying essential oils by distillation in steam is said to be of acid v. 5.31; sap. v. 210.85; i.v. (Hübl) 67.94; and to contain 84.69 per cent. insoluble fatty acids yielding 58.5 per cent. liquid fatty acids. (See Umbellularia Oil, and Lauric Acid.)

**LAUREN'T'S ACID** — See Acid, Laurent's.

**LAURIC ACID (Dodecanoic Acid)** ( $C_{11}H_{23}.COOH$ ) — A member of the normal fatty acid series and a notable constituent of oil of laurels or fat of the bay-tree (*Laurus nobilis*). It can also be obtained from pichurim beans, coconut and other oils; it melts at 47° C., and is soluble in hot alcohol.

**LAURITE** — See Ruthenium.

**"LAUSETO NEU"** — An insecticidal preparation developed in Germany during World War II. The active principle is reported to be chlorophenyl chloromethyl sulphone ( $ClC_6H_4SO_2CH_2Cl$ ). See "New Synthetic Contact Insecticides," by Busvine (*Nature*, 158, 22 (1946)).

**"LAUTAL"** — An aluminium-silicon-(2 per cent.) copper (4 per cent.) alloy, more resistant to corrosion than aluminium, with a tensile strength of 40 kg. per sq. mm. and a Brinell hardness of 88; it resembles "Duralumin" in many respects.

**LAVA** — See Pumice-Stone.

**LAVENDER OIL** — The essential oil distilled from the flowers of *Lavandula officinalis*, cultivated in England and France. It is colourless or pale yellow and possesses a more fragrant odour than oil of spike lavender; sp. gr. 0.882 to 0.890 at 15° C.; opt. rot. -3° to -10°; ref. ind. 1.459 to 1.470 at 20° C.; soluble in alcohol and ether. It contains about 60 per cent. of linalool, 21 to 45 per cent. of linalyl acetate, and small amounts of geraniol and cineol.

**LAVENDER (SPIKE) OIL** — The essential oil distilled from the flowers of *Lavandula latifolia* and other species of *Lavandula*, growing in the lower mountainous districts of France, Spain, and Italy. It is colourless or pale yellow; sp. gr. 0.900 to 0.920 at 15° C.; opt. rot. -4° to +6°; ref. ind. 1.462 to 1.469 at 20° C.; soluble in alcohol and ether. It contains about 30 per cent. of cineole, with linalool, camphor,

borneol, and terpineol. A description of the oil obtained from *Lavandula delphinensis* is given by L. Bénézet in *Parfumerie*, 1, 235 (1943); and of the oil from *Lavandula pedunculata* by J. Gattefosse and G. Igolen in *Parfumerie*, 1, 97 (1943).

**LAWSONITE** — A mineral double silicate of calcium and aluminium ( $\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$ ); crystal system No. 4, and sp. gr. 3.1.

**LAZULITE** — A mineral crystalline form of hydrated phosphate of aluminium, magnesium and iron found in Styria, Brazil, N. Carolina, etc.; sp. gr. 3.0. A specimen from Graves Mountains (Georgia) has been described as calcium lazulite, corresponding to the formula  $(\text{Fe}, \text{Mg}, \text{Ca}) \text{O}, \text{Al}_2\text{O}_3, \text{P}_2\text{O}_5, \text{H}_2\text{O}$ .

**LEACHING** — The washing out or extraction, or lixiviation of soluble constituents from metalliferous or other insoluble parts of substances. The process is used, for example, in the extraction of sodium nitrate from caliche, the treatment of cupreous pyrite for the extraction of associated metals, and the extraction of tanning and dye materials, by such appliances as the Thornycroft patent apparatus. (See Extraction.)

**LEAD (Pb) and its Compounds** — Atomic weight, 207.21. See Elements for other data. Lead occurs naturally, for the most part, in the form of *galena* (*galenite*) or lead sulphide ( $\text{PbS}$ ), in the U.S.A., Australia, Mexico, Bolivia, Upper Silesia, and Spain, the British production, once considerable, being now almost a negligible factor, and the U.S.A. the largest producer. It also occurs as carbonate ( $\text{PbCO}_3$ ) in *cerussite* (white-lead ore) in Cornwall, Cumberland, Scotland, Mexico, and some of the U.S.A.; as sulphate ( $\text{PbSO}_4$ ) it is present in *anglesite*; in *lanarkite* as a basic sulphate ( $\text{PbSO}_4, \text{PbO}$ ) or ( $\text{PbSO}_4, \text{PbCO}_3$ ); in *massicot* (found in the U.S.A.) as monoxide ( $\text{PbO}$ ); in *mallockite* as basic chloride ( $\text{PbCl}_2, \text{PbO}$ ), etc.; large quantities of lead vanadate (*vanadinite*) are found in the Transvaal and at Tsumeb, whilst a rich mine exists in Burma.

The metal is produced by several processes, one of which consists in roasting lead sulphide in a reverberatory furnace at a certain temperature, whereby some of it is oxidized into lead sulphate ( $\text{PbSO}_4$ ) and some into lead oxide ( $\text{PbO}$ ), a part of the sulphur being burnt off as sulphur dioxide ( $\text{SO}_2$ ). Upon increasing the temperature, a further change takes place in the mixture which still contains some lead sulphide, and metallic lead results from the two interactions:  $\text{PbSO}_4 + \text{PbS} = 2\text{Pb} + 2\text{SO}_2$ , and  $2\text{PbO} + \text{PbS} = 3\text{Pb} + \text{SO}_2$ ; that is to say, the rest of the combined sulphur is burnt off, and the metallic lead thus produced is subsequently refined. By another method the ore is smelted with coke and iron or a suitable iron ore, whereby iron sulphide is formed as a regulus, which floats over the metallic lead which is thus set free. The associated metallic impurities (antimony, tin, copper, etc.) are removed by oxidation in a reverberatory furnace, collecting in a dross on the surface of the lead. Silver, when present, is later removed by a process to be described. In other metallurgical processes, a

saturated solution of salt (which is a good solvent for lead chloride and lead sulphate) is used, and from the solution so obtained (when not contaminated with other elements) the oxide is precipitated by the action of lime, or (when contaminated with other elements) by electrolysis, the metallic lead being obtained from the oxide by reduction.

## LEAD, WORLD SMELTER PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country				Smelter Lead Metric Tons	
Germany-Austria	..	..	..	178,000	
Belgium	..	..	..	95,000	
Italy	..	..	..	40,000	
France	..	..	..	40,000	
Spain	..	..	..	31,000	
Poland	..	..	..	19,000	
United Kingdom	..	..	..	12,000	
				<hr/>	415,000
U.S.S.R.	..	..	..		66,000
U.S.A.	..	..	..	386,000	
Mexico	..	..	..	236,000	
Canada	..	..	..	145,000	
				<hr/>	767,000
Peru	..	..	..	24,000	
Argentina	..	..	..	11,000	
				<hr/>	35,000
Burma	..	..	..	78,000	
Japan	..	..	..	13,000	
				<hr/>	91,000
Tunisia	..	..	..		24,000
Australia	..	..	..		243,000
					<hr/>
Sum of above	..	..	..		1,641,000
WORLD PRODUCTION	..	..	..		1,693,000

In addition to the above-named countries lead is smelted in mentionable quantity in China, Czechoslovakia, Greece, Rumania, South-West Africa, Yugoslavia.

Acid lead fluosilicate is used as an electrolyte in the Betts electrolytic lead-refining process, the hydrofluosilicic acid required being preferably made by retorting a mixture of high-grade fluorspar and sulphuric acid and passing the hydrogen fluoride (HF) gas into water containing finely crushed quartz or silica in suspension, by which means a solution containing about 33 per cent. hydrofluosilicic acid ( $\text{H}_2\text{SiF}_6$ ) is obtained. If inferior fluorspar be employed in the retorting process, silicon fluoride ( $\text{SiF}_4$ ) gas accompanies the hydrogen fluoride gas, but is also resolved into  $\text{H}_2\text{SiF}_6$  in contact with water, accompanied by gelatinous  $\text{SiO}_2$ ; but this modification of the process is not so economical.

The process used for the desilverization of lead is based upon the use of zinc, which, when mixed in a molten state with argentiferous metal, solidifies first, and abstracts the greater part of the silver. It is, however, the undesilverized lead, otherwise known as "chemical lead," which is used in the forms of pipes and sheets and for lining tanks so extensively in chemical industries. The B.S.I. (B.E.S.A.) specification of "chemical lead" gives its content as 99.99, but if copper be present the lead content may be reduced to the extent of the copper content. The presence of the small content of copper is considered by some as an advantage, while the small percentages of other metals (silver and bismuth) are negligible.

Studies of the radioactive disintegrations of uranium and thorium show that the ultimate product of every series is lead. Investigations of metallic lead as obtained from radioactive minerals, that is, minerals containing uranium and radium, have led to the view that there are at least three isotopes. The end-product of the uranium-radium series is lead of atomic weight 206, and of the thorium series 208, the atomic weight of ordinary lead being 207.2. Atomic weight determinations by T. W. Richards in 1916 showed lead from uranite of North Carolina of atomic weight 206.40, from carnotite of Colorado 206.59, and from pitchblende of Joachimsthal 206.57. Baxter and Bliss found that uranium lead extracted from Swedish kolm showed atomic weight of 206.01. Lead prepared from a Norwegian thorite (from Langesundfjord) (containing 30.1 per cent. thorium, 0.45 per cent. uranium, and 0.35 per cent. lead) showed atomic weight of 207.77, and another prepared from Ceylon thorite gave the atomic weight of 207.74 (Soddy and Hyman). F. W. Aston in *Proceedings of the Royal Society*, **A140**, 535 (1933) reported, from a study of the mass-spectrograph of lead, the existence of four isotopes, namely, of mass 208 (50.1 per cent.), 207 (20.1 per cent.), 206 (28.3 per cent.), and 204 (1.5 per cent.), which data were accepted by the International Committee on Stable Isotopes. Apparently, isotope of mass 204 is not produced in radioactive changes, but is found only in ordinary lead. In a paper in *J. Amer. Chem. Soc.*, **60**, 1571 (1938), A. O. Nier reports the isotope abundance of ordinary lead from 12 mineral specimens, for 9 of which there are atomic weight determinations. The relative abundances of the isotopes "vary considerably in spite of a nearly constant atomic weight." He found no trace of isotopes 210, 209, 205, and 203. (See Frontispiece for current values.)

Lead is a bluish-white metal having a high specific gravity, low melting point, remarkable plasticity, and excellent resistance to corrosion. In the form of sheet it finds a wide use in the construction of chemical plant, roofing, and sound-proofing. As pipe, it is used for transporting water and chemicals and for cable-sheaths. Other uses are in foil, collapsible tubes, lead weights, and ammunition. It has been reported that lead filings, made with a coarse rasp, sprinkled on the threads of piping and held together by the cutting oil remaining on the threads, makes a better joint than that obtainable by the use of white-lead.

Lead alloys with many metals, the most commonly used component being antimony. The antimonial leads are well known for their physical properties. They are used for storage-battery grids, die castings, in the form of sheets in building construction, in shrapnel, collapsible tubes, and cable sheaths.

*Type-metal* consists, in part, of lead (alloyed with antimony and tin), and lead is also used in the manufacture of *fusible metal* and *pewter*; *solder*, as used by plumbers and tin-plate workers, is a mixture of lead and tin in proportions varying with the particular applications to be made of it; whilst so-called *pot-metal* is an alloy of lead and copper.

Tree-lead and "spongy lead" are names given to that form of the metal resulting from the electrolysis of a lead solution (in arborescent crystalline form at the negative electrode). It can also be obtained by deposition on a bar of zinc placed in an aqueous solution of a lead salt.

Lead coatings on steel received attention because of war-time shortages in tin and zinc for this purpose. Both hot-dipped and electrolytic processes were employed and the results often proved superior in that coated products were economical, easily workable, and resistant to corrosion. (See papers by C. H. Hack, D. S. Kondrat, and H. E. Zahn (*Metal Progress*, **46**, 718 (1944)); by H. A. Knight (*Metals and Alloys*, **20**, 1296 (1944); and by J. L. Bray (*Steel*, **115**, 110 (Dec. 18, 1944).) Small amounts of lead are sometimes added to steels and to certain non-ferrous alloys to improve machinability.

See "Lead-Lined Equipment," by E. Mantius and H. F. Freiherr (*Ind. Eng. Chem.*, **29**, 373 (1937); *The Ternary Alloys of Lead: Their Use in Building*, by Dept. of Sci. and Ind. Research (H.M. Stationery Office); *Metals*, Vol. II, by H. Carpenter and J. M. Robertson (Oxford University Press); *Lead*, by J. A. Smythe (Longmans, Green and Co., London); *Metallurgy of Lead*, by H. O. Hofman (McGraw-Hill Book Co., New York); and *Lead and Copper Smelting*, by H. W. Hixon (Hill Publishing Co., New York).

**White Lead**, which is used so much in compounding paints and putty, is a mixture of lead carbonate and hydrated lead oxide.

Of the various processes for making white-lead, the oldest and most extensively used is the so-called Dutch process, which depends upon the use of acetic acid in association with moist air and carbon dioxide. The lead, prepared in a way to present as large a surface as possible by being cast into rough gratings or grids, is placed on pots over a  
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bed of spent tan-bark, acetic acid of 3 to 5 per cent. strength being placed in the pots. The acid is slowly vaporized by the heat of the fermenting tan, and this, acting upon the lead, forms a compound basic acetate, which undergoes further changes by the carbon dioxide evolved from the fermenting tan, and the action of air and moisture, finally resulting in the production of white-lead of commerce ( $2\text{PbCO}_3$ ,  $\text{Pb(OH)}_2$ ).

There is an electrical process of producing white-lead in which an aqueous solution of sodium acetate is electrolysed between an anode of lead and a cathode of iron or copper separated by a diaphragm, while carbon dioxide is bubbled in at the cathode. The anolyte contains a small quantity of sodium carbonate or lead acetate and the catholyte a soluble carbonate or hydroxide. Acetic acid is set free at the anode and becomes lead acetate; sodium hydroxide produced at the cathode is carbonated by the carbon dioxide, and by interaction of these products white-lead is formed and the sodium acetate is recovered. Finely divided litharge is made, by the Sacher patent, into a stiff paste with water or dilute solution of ammonia, and a mixture of ammonia and carbon dioxide gases is passed through at the ordinary or increased pressure. The ammonia is stated to act only as a carrier for the carbon dioxide and water to the lead oxide.

A promising line of improvement in the manufacture consists in the employment of mechanical means for agitating the metallic lead in finely comminuted form in the presence of carbon dioxide and dilute acetic acid, the mass being kept always moist by careful addition of the liquid reagent.

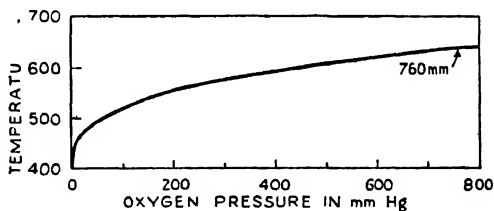
Among many other processes for making "white-lead" is that of burning galena or other suitable material with coke and flux in a furnace, and cooling and collecting the white-fume product, which is used as a substitute for the ordinary article. B. S. White, of Joplin, Missouri (U.S.A.), has patented an improvement on this process in which molten lead is blown by means of compressed air in an atomized state with a mixture of sulphur dioxide, air, and natural gas, thereby producing a fume of super-sublimed white-lead consisting of 25 per cent.  $\text{PbO}$  and 75 per cent.  $\text{PbSO}_4$  ( $\text{PbO}$ ,  $2\text{PbSO}_4$ ), although the chemical composition of the product may be changed within certain limits at the will of the manufacturer. This product is alleged to be equal or superior to the basic carbonate for some purposes, and can be more particularly used in making ready-mixed paints.

White-lead paint has excellent covering power and may be prepared by grinding the dry white-lead in linseed oil or oil and turpentine admixed. It can also be made from the wet pigment by first of all grinding the dry base in water, thus obtaining a paste retaining from 40 to 60 per cent. water, which is subsequently well mixed by agitation or grinding with slightly heated refined raw linseed oil. The oil replaces the water, which rises to the top after settlement and can then be drawn off, leaving only a few tenths of 1 per cent. in the paste, which is again thoroughly ground. With respect to white-lead poisoning, an amount greater than 2 grains per day is viewed as dangerous for a man

to absorb. No plumbiferous vapour is given off from lead paint; the danger arises from inhalation of the dust when paint is rubbed down dry, and this can be obviated by use of wetted water-proof sandpaper. (See Turpentine.) Mixed with boiled linseed oil, white-lead makes a useful cement for pipes. (See Paints.)

**Lead Oxides**—Five oxides of lead are known, all of which are insoluble in water: suboxide ( $\text{Pb}_2\text{O}$ ), monoxide ( $\text{PbO}$ ), sesquioxide ( $\text{Pb}_2\text{O}_3$ ), trilead tetroxide ( $\text{Pb}_3\text{O}_4$ ), and dioxide ( $\text{PbO}_2$ ). Of these the  $\text{PbO}$  (litharge) and the  $\text{Pb}_3\text{O}_4$  (red-lead) are the more important.

$\text{Pb}_3\text{O}_4 \rightleftharpoons 3 \text{PbO} + 0.5 \text{O}_2$  REACTION  
OXYGEN PRESSURE—TEMPERATURE RELATIONSHIP



**Lead Monoxide** is known in red and yellow forms (being polymorphic modifications). It is commonly prepared by strongly heating the metal in air, or by roasting nitrate or carbonate of lead. Under the name of *litharge*, it is used in the manufacture of certain qualities of glass and pottery, acid-resisting cements, lutes, and lakes, and in connection with that of oils, varnishes, and the leather and tanning trades. *Massicot* is native lead monoxide, of specific gravity 9.3.

**Red-Lead (Minium)** results from the prolonged heating of the monoxide in contact with air at about  $450^\circ \text{C}$ ., and is a scarlet-coloured powder, which varies to some extent in colour and composition as prepared for commercial uses, containing as it does varying proportions of other oxides of the metal. It also occurs in natural deposits. It is largely used in the manufacture of ceramics, flint glass, for making a useful cement in admixture with boiled oil, and as a pigment.

**Lead Dioxide (Peroxide)** is a brown, crystalline body prepared amongst other methods by addition of calcium hypochlorite to an alkaline emulsion of lead hydroxide, and also by separation of the residue of lead dioxide after heating trilead tetroxide and nitric acid (lead nitrate formed in solution). By combination with alkalis, so-called plumbates are produced, such as potassium plumbate ( $\text{K}_2\text{PbO}_3$ ) and calcium plumbate ( $\text{CaPbO}_3$ ). The dioxide finds use as an oxidizing agent. It decomposes, upon heating, into red oxide ( $\text{Pb}_3\text{O}_4$ ) and at higher temperature into yellow oxide ( $\text{PbO}$ ).

A **Lead Hydroxide** of indefinite composition, but approximating to  $2\text{PbO} \cdot \text{H}_2\text{O}$ , is produced in the form of a white, bulky precipitate by adding an alkaline hydroxide solution to one of a lead salt.

**Lead Chloride** ( $\text{PbCl}_2$ ) is a white, crystalline substance, which is

precipitated in a curdy form from solutions of lead salts by the addition of hydrochloric acid or a solution of a chloride, and can be obtained by dissolving the monoxide or lead carbonate in hot hydrochloric acid, from which solution it crystallizes out on cooling in long lustrous needles. It is soluble in boiling water (1 part in 25 parts).

A hydrated oxychloride, known as "Pattinson's white-lead," is obtained by heating lead chloride in air, and has a composition approximating to  $\text{PbCl}_2 \cdot \text{PbO} \cdot \text{H}_2\text{O}$ .

**Lead Sulphate** ( $\text{PbSO}_4$ ) is a white, insoluble body produced as a by-product in the manufacture of aluminium acetate (for use in water-proofing tarpaulins, etc.), and also results from the precipitation of lead salts in solution, by sulphuric acid or solution of a sulphate. Basic lead sulphate is used in compounding paints.

**Lead Nitrate** ( $\text{Pb}(\text{NO}_3)_2$ ), a crystalline substance, very soluble in water, is made by dissolving litharge in nitric acid, and finds industrial applications as a mordant, in pigment compounding, etc.

**Lead Iodide** ( $\text{PbI}_2$ ) is a beautiful yellow insoluble compound used in photography, bronzing, printing, etc.

**Lead Sulphide** ( $\text{PbS}$ ) is a black compound found native as *galena* (*galenite*), and can be prepared by the action of hydrogen sulphide upon solutions of lead salts. It is insoluble in water, and used in ceramics.

**Lead Chromate (Leipzig Yellow)** ( $\text{PbCrO}_4$ ), found in mineral form as *crocoite*, is a beautiful chrome-coloured insoluble pigment; used also in match-making.

**Lead Acetate (Sugar of Lead)** ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ ) is a white, crystalline, poisonous salt, soluble in water; it becomes anhydrous when heated to  $75^\circ \text{C}$ ., and is made by the action of acetic acid on litharge. It is used in dyeing and printing cotton goods, in varnish-making, the enamel industry, and medicine, and is prepared commercially in a number of grades of varying colour (white, grey, and brown) and purity. There are other acetates—viz. the monobasic salt ( $\text{Pb}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_2$ ) and the tribasic ( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{PbO} \cdot \text{H}_2\text{O}$ ), both of which find industrial applications, the last named being used in weighting silk and textile printing.

**Lead Antimonate (Naples Yellow)** ( $\text{Pb}_3(\text{SbO}_4)_2$ ) is insoluble in water, and is used as a pigment, also for staining glass and china ware.

**Lead Arsenate** ( $\text{Pb}_3(\text{AsO}_4)_2$ ) is a white, insoluble, crystalline body used in compounding insecticides and fungicides. It is stated that the commercial material may contain two compounds, namely, lead hydrogen arsenate,  $\text{PbH}(\text{AsO}_4)$ , and a basic arsenate ( $\text{Pb}(\text{PbOH})(\text{AsO}_4)\text{H}_2\text{O}$ ). The most widely used procedure for making this compound is that in which lead oxide is suspended in a weak solution of arsenic acid with a small amount of nitric or acetic acid as a catalyser.

**Lead Borates** — The various borates of lead that have been described appear to be basic substances of varying composition. One such is the compound formulated as  $(\text{Pb}(\text{BO}_2)_2 \cdot \text{H}_2\text{O})$ , which is insoluble in water and used in the varnish and paint trades as a drier.

**Lead Carbonate** ( $\text{PbCO}_3$ ) is a white, crystalline powder, insoluble in water, used in paint-making and the ceramic industries.

**Lead Oleate** ( $\text{Pb}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$ ) is a white, unctuous substance, soluble in alcohol, ether, benzol, and turpentine, used in making certain varnishes and lacquers and as a paint drier.

**Lead Silicate** ( $\text{PbSiO}_3$ ) is a white, crystalline, insoluble compound used as a glaze in ceramics and for fireproofing fabrics.

**Lead Cyanide** ( $\text{Pb}(\text{CN})_2$ ) is used in metallurgy.

**Lead Azide** ( $\text{Pb}(\text{N}_3)_2$ ), prepared by precipitation from a mixture of solutions of sodium azide and lead nitrate or acetate, is used as a fulminating or detonating agent in preference to fulminating mercury, since it contains more nitrogen, and is a better initiator, although not so sensitive to blows or percussion. It detonates at  $327.5^\circ \text{C.}$ , whereas fulminating mercury detonates at  $215^\circ \text{C.}$  It is also used as a priming agent for fulminates, and is comparatively safe when in a state of fine division, although large crystals are very dangerous. (See Azides.)

**Lead Resinate**, prepared by heating a mixture of lead acetate solution and rosin oil or resin, is used as a varnish drier.

**Lead Stearate** ( $\text{Pb}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$ ), made from lead acetate and sodium stearate, is also used as a drier.

**Lead Aluminate** ( $\text{PbO}, \text{Al}_2\text{O}_3$ ) — A useful white pigment. (See Paints.)

**Lead Titanate** — A resistant pale yellow pigment. (See Paints.)

**Lead Soaps** — See Lead Plaster.

**Lead Tetraethyl** — See Motor Spirit.

All lead compounds are poisonous, but lead glazes of low solubility as used in the pottery industry are practically innocuous.

**LEAD ASHES** — The skimmings due to oxidation in melting down lead.

**LEAD PLASTER** — A mixture of lead soaps of fatty acids, prepared by heating olive oil with litharge or by heating a solution of lead nitrate with sodium linoleate. Used as a drier in varnish-making.

**LEATHER** — See Tanning.

**LEATHER CLOTHS** are made by coating textile fabrics with various mixtures of materials. The various makes include "Fabrex," "Fabri-koid," "Pegamoid," "Rexine," "Stipplex." (See also Tanning.)

**LEATHER JAPANING** — See Tanning.

**LEAVEN** is really bread which has commenced to decompose by a sort of fermentation, but its use for leavening fresh bread has been superseded by the general use of yeast. (See Yeasts.)

**LEBLANC PROCESS** — See Sodium (Carbonate).

**LECITHIN** — A monoaminomonophosphatide; also represented as a triglyceride containing two complex acyl groups, derived from stearic, oleic, and other acids, the third hydrogen being replaced by a choline-phosphoric group. Lecithin of egg yolk is sometimes used in compounding margarine. Some synthetic lecithins have been prepared, including the stearic and palmitic compounds. The phosphatides of soy lecithin are prepared in molecular dispersion in water (lecithin

hydrate or "Aqualoid"). (See "Lecithin as an Emulsifier," by R. M. Woodman (*J.S.C.I.*, **51**, 95 T (1932)); "The Nature, Preservation and Uses of Lecithin," by Frydlander (*Rev. Prod. Chim.*, **50**, 145 (1947)); Brain Matter, and Eggs.)

**LEGUMIN (Vegetable Casein)** — The distinctive nutritive protein constituent of peas, beans, and lentils, amounting to about 25 per cent. calculated on the dried products. (See Albumins, and Proteins.)

**LEIPZIG YELLOW** — Lead Chromate. (See Chrome Yellows.)

**LEMON GRASS OIL (Indian Oil of Verbena, Indian Melissa Oil)** — An essential oil, distilled from *Cymbopogon flexuosus* (East Indian and West Indian varieties), or from *Cymbopogon citratus* (Ceylon and Straits Settlements). It contains from 75 to 85 per cent. of citral and is a reddish-yellow oil; soluble in alcohol and ether; sp. gr. 0.895 to 0.908 at 15°C.; opt. rot.  $-4^{\circ}$  to  $+1^{\circ}$ ; ref. ind. 1.483 to 1.489 at 20°C. Trinidad lemon grass oil has been examined by D. J. Cosgrove and H. T. Islip, *Bull. Imp. Inst.*, **44**, 290 (1946), and found to compare favourably in odour, citral content, and solubility with other varieties. (See Verbena Oil.)

**LEMON OIL** — The essential oil obtained by expression from the peel of *Citrus Limonia* (Fam. Rutaceæ) in which it is present to the extent of about 1 per cent. It is a pale yellow limpid oil, having a lemon odour and containing about 90 per cent. of *d*-limonene, associated with phellandrene, citral (about 4 per cent.), and citronellal; sp. gr. 0.857 to 0.861 at 15°C.; opt. rot.  $+57^{\circ}$  to  $+65^{\circ}$ ; ref. ind. 1.474 to 1.476 at 20°C.; soluble in alcohol and ether. It is used as a flavouring agent and in perfumery.

**LENTILS** — Seeds of the leguminous annual plant *Ervum lens*, from which a flour can be prepared. There are several varieties extensively cultivated in European countries.

**LEPIDOLITE (Lithia Mica)**  $((\text{LiK})_2\text{Al}_2\text{O}_3(\text{F},\text{OH})_2,3\text{SiO}_2)$  — A Moravian purple mineral of crystal system, No. 5, and sp. gr. 2.8 to 3.0, containing lithium and aluminium in combination as silicates. (See Cesium, Mica, Potassium, and Rubidium.)

**LEPTAZOL ("Cardiazol," "Hexazole," "Metrazol," "Phrenazol," "Triazol")**  $(\text{C}_6\text{H}_{10}\text{N}_4)$  — A colourless, odourless crystalline compound,

namely, pentamethylenetetrazole,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N} \cdot \text{C} \cdot \text{N} \cdot \text{N} \cdot \text{N}$ ;

prepared by interaction of hydrazoic acid and cyclohexanone in cold benzene solution; freely soluble in water; soluble in alcohol, ether, and chloroform; m.p.  $57^{\circ}$  to  $60^{\circ}$  C. It is used in medicine as a stimulant in cardiac failure, respiratory failure during anaesthesia, and in narcotic poisoning. In large doses, it is used to produce convulsions for the shock treatment of mental conditions such as schizophrenia. For an account of its pharmacological action, see M. Chakravarti in *J. Pharmacol.*, **67**, 153 (1939); and R. W. Whitehead and W. B. Draper in *Surg. Gynec. Obstet.*, **74**, 1024 (1942).

“**LETHANE**” — Trade name for several organic thiocyanates, used as insecticides.

“**LEUCARSONE**” — See Carbarsone.

**LEUCINE (Alpha-Aminoisohehoic Acid)**  $((\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CH}(\text{NH}_2).\text{COOH})$  — The first amino-acid to be isolated, by Proust in 1818, and formed as a hydrolytic product of proteins. It is a white powder, of melting point approximately  $293^\circ\text{C}$ ., and a hydrolytic product of the antibiotic Gramicidin S.

**LEUCITE** — A mineral double silicate of aluminium and potassium ( $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$ ), of rock character, found in Wyoming (U.S.A.) and in Italy. Leucite has been proposed as a source of potash in the United States, and is used as such a source in Italy, where it is also used for the preparation of “Rhenania phosphate,” by heating with phosphatic minerals to  $1,250^\circ\text{C}$ ., the product being an alkaline fertilizer soluble in citric acid, etc. It is found in crystal systems No. 1 and No. 4, having a sp. gr. of about 2.5, and can be separated electromagnetically from the basaltic (laval) masses of volcanoes which contain it. It is treated with hydrochloric or nitric acid, the products being silica and a solution of aluminium and potassium chlorides or nitrates. (See Aluminium, and Potassium.)

**LEUCO-BASES** — See Dyes.

**LEUCOCYTES** — See Bacteria, and Phagocytes.

**LEVIGATION** — The reduction of lumps and hard parts of substances to pulverulent form by grinding in water or other liquid. (See Leaching.)

**LEVOROTATORY** — See Polarization.

**LEVULINIC ACID (Acetopropionic Acid)**  $(\text{CH}_3\text{CO}(\text{CH}_2)_2\text{COOH})$  — A colourless to white solid, of m.p.  $33.5^\circ\text{C}$ ., of b.p.  $245^\circ\text{C}$ ., very soluble in water, alcohol, and ether, and formed by oxidation of levulose.

**LEVULOSE (Lævulose, Fructose)** — See Fructose.

“**LEXONE**” (Du Pont) — Trade-mark for benzene hexachloride insecticide. Used for controlling grasshoppers, boll weevil, green bug, lice, ticks, horn flies, and mange.

**LEY** — See Lye.

**LICHENIN (Moss Starch)** — A polysaccharide resembling starch present in many lichens, e.g., Iceland Moss (*Cetraria islandica*), and serving as food material.

**LICHENS** — Many species of these plants are used for food and in dyeing. In the varieties *Rocella*, *Lecanora*, and *Evernia prunastri*, lecanoric and evernic acids occur; these so-called depsides are related to gallotannin. The vegetable colours litmus and archil are depsides obtained from lichens. A compound named lichenol, of m.p.  $72^\circ$  to  $73^\circ\text{C}$ ., is reported to be the chief constituent of oak-moss (*Evernia prunastri*) oil. (See Fungi, and Orcinol.)

**LICORICE** — See Liquorice.

**LIEBIG'S BULBS** — See Organic Analyses.

**LIEBIG'S CONDENSER** — A simple form of glass-tube condenser, part of the tube being surrounded by a larger tube, and through the annular space between the tubes water for cooling the inner tube is circulated from bottom to top.

**LIGHT (Photochemical Aspects)** — Some chemical reactions are induced by radiation. Examples are: the image on a photographic film or plate; the fading of dyes in sunlight; the ageing of paint; the use of blue-printing process paper; the explosion of hydrogen and chlorine gases when subjected to sunlight; the transformation of carbon dioxide and water into carbohydrates and oxygen by means of the chlorophyll in the green leaves of plants. The inducing or activating wave lengths are commonly within the range of 2,000–8,000 Angstroms (1 Angstrom =  $10^{-8}$  cm.). 2,000–3,940 A.U., ultra-violet; 3,940–7,500 A.U., visible; 7,500 A.U., infra-red (see Wave Lengths). The contrasting type of reaction wherein light is generated by chemical reactions—chemiluminescence—is illustrated by: the burning of substances, especially magnesium and aluminium, the light from which is notably rich in actinic rays; the luminosity of the firefly and that caused by the decaying of certain organic matter; the glowing of yellow phosphorus in air; the green glow of magnesium *p*-bromophenyl bromide dissolved in ether when exposed to air.

By contrast the following manifestations are physical rather than chemical. Fluorescence is the property possessed by some substances of emitting visible light while exposed to the action of radiation of a different wave length than the emitted light as in fluorescent lamps, fluoroscopic examination by X-rays, fluorite mineral when exposed to ultra-violet light, eosin, or fluorescein in water solution in visible light, and riboflavin dissolved in chloroform in ultra-violet light (a quantitative method of analysis). Phosphorescence is shown by specially prepared calcium, strontium, and barium sulphides when they continue to emit light after the incident light has been cut off—so that after exposure to light they shine in the dark. Radium salts also emit a visible glow in the dark.

Whenever a photochemical reaction occurs it is associated with radiation of a definite wave length or intensity. Thus in the photochemical reactions:

- (1)  $2\text{HI} = \text{H}_2 + \text{I}_2$  light of wave length 2,800–3,000 Angstroms is required.
- (2)  $\text{H}_2 + \text{Cl}_2 = 2\text{HCl}$  light of wave length 4,000 Angstroms is required.
- (3)  $3\text{O}_2 = 2\text{O}_3$  light of wave length 1,700–1,900 Angstroms is required.

The generalizations connecting wave lengths of the light absorbed and the photochemical change produced are generally known as:

(1) *Grotthus and Draper Law*: Only radiations which are absorbed by the substance are effective in producing chemical change. It does not follow that all the light which is absorbed is effective chemically,

some of it may be converted into heat or re-emitted as light of the same or of another wave length.

(2) *Stark-Einstein Law* : Each molecule taking part in the primary photochemical reaction absorbs one quantum of radiation. The energy of this quantum is given by the relation :  $e=h\nu$ , where  $e$ =the energy in the quantum expressed in ergs,  $h$ =Planck constant ( $6.62 \times 10^{-27}$  erg  $\times$  seconds),  $\nu$ =frequency of the radiation and is related to the wave length by  $\nu=\frac{c}{\lambda}$ , where  $c$ =velocity of light ( $3 \times 10^{10}$  centimetres per second),  $\lambda$ =wave length of the radiation expressed in centimetres (1 Angstrom= $10^{-8}$  cm.). If one gram mole of substance is considered instead of one molecule, then the relation becomes :  $E=Nh\nu$ , where  $N$ =Avogadro number ( $6.02 \times 10^{23}$  molecules per gram mole),  $E$ =the energy per gram mole of absorbed radiation and is called the "Einstein." This can be illustrated by the example of the photochemical decomposition of hydrogen iodide gas where  $2\text{HI} + N h \nu = \text{H}_2 + \text{I}_2$ , and is to be read : Two gram moles of hydrogen iodide plus one Einstein of radiation of the proper frequency will yield one gram mole of hydrogen plus one gram mole of iodine.

Many overall photochemical reactions do not follow the Stark-Einstein relationship but show a quantum yield (quantum yield=number of gram moles reacting  $\div$  number of Einsteins absorbed) other than one, thus, when hydrogen and chlorine gases are mixed and subjected to radiation having a wave length of 4,000 Angstroms, one Einstein of absorbed radiation causes not one but  $10^5$  gram moles to react in a chain reaction ; and in the photochemical decomposition of hydrogen iodide the quantum yield is two.

The following table lists some typical photochemical reactions, the wave lengths of the radiation associated with the particular reaction, and the accompanying quantum yields :

Reaction	Wave Lengths Approx. Angstroms	Quantum Yield, Approx.
$2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$ .. ..	2,100	0.2
$2\text{C}_{14}\text{H}_{10} = \text{C}_{28}\text{H}_{20}$ .. ..	3,400	1
$(\text{CH}_3)_2\text{CO} = \text{CO} + \text{C}_2\text{H}_6$ .. ..	2,500	1
$\text{SO}_2 + \text{Cl}_2 = \text{SO}_2\text{Cl}_2$ .. ..	4,200	1
$\text{H}_2\text{S} = \text{H}_2 + \text{S}$ .. ..	2,100	1
$2\text{Fe}^{++} + \text{I}_2 = 2\text{Fe}^{+++} + 2\text{I}^-$ .. ..	5,800	1
$2\text{NO}_2 = 2\text{NO} + \text{O}_2$ .. ..	3,600	1.5
$2\text{HI} = \text{H}_2 + \text{I}_2$ .. ..	3,000	2
$3\text{O}_2 = 2\text{O}_3$ .. ..	1,800	3
$n\text{C}_2\text{H}_2 = (\text{C}_2\text{H}_2)_n$ .. ..	2,000	7
$\text{CO} + \text{Cl}_2 = \text{COCl}_2$ .. ..	4,000	10
$\text{Cl}_2 + \text{H}_2 = 2\text{HCl}$ .. ..	4,000	10

In general a photochemical reaction is activated only by that radiation whose minimum energy is as great or greater than the corresponding thermochemical reaction (see Table below), for example, thermochemical studies of the photosynthetic reaction,  $6\text{CO}_2 + 6\text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ , show that the absorption of 112,000 calories per gram atom of carbon, as carbon dioxide, is utilized. In the absence of chlorophyll, this energy can only be supplied by radiation of 2,300 Angstroms or less. When, however, radiation of 2,300 Angstroms or less is not available, as in the sunlight that reaches the surface of the earth, then chlorophyll enables this reaction to proceed with the longer wave lengths. When sunlight is used as the source of light it is found that the highest rate of photosynthesis is produced by light from the red end of the spectrum (the longer wave lengths). This corresponds to the absorption resulting upon passing sunlight through a solution of chlorophyll.

TABLE SHOWING THE RELATIONSHIP BETWEEN WAVE LENGTHS AND ENERGY

Colour of Radiation	Wave Length of Radiation Approx. Angstroms	Energy of One Einstein Approx. Calories
Red .. .. .	7,000	40,000
Orange .. .. .	6,200	45,000
Yellow .. .. .	5,800	48,000
Green .. .. .	5,300	53,000
Blue .. .. .	4,700	60,000
Violet .. .. .	4,200	67,000
Ultra-violet .. .. .	2,000	142,000

F. Weigert in 1907 observed that, in the presence of chlorine, the photochemical reactions between sulphur dioxide and oxygen, between hydrogen and oxygen, the decompositions of phosgene, and the decomposition of ozone, occurred under the influence of blue or violet radiation. In the absence of chlorine, blue and violet radiation had little or no effect upon the same reactions. He explained this phenomena on the assumption that the chlorine acted as a radiation absorbing sensitizer which made it possible for the blue or violet radiation to activate the photochemical reaction. Many other substances have this ability to sensitize photochemical reactions, and a few examples are :

(1) Mercury vapour sensitizes the following reactions : (a) dissociation of hydrogen ; (b) combination of hydrogen and oxygen to form hydrogen peroxide ; (c) interaction of hydrogen and ethylene to form ethane ; (d) interaction of hydrogen and carbon monoxide to form formaldehyde ; (e) decomposition of ammonia.

(2) Chlorophyll acts as a sensitizer for the interaction of carbon dioxide and water to form carbohydrates and oxygen and this reaction

is endothermic, absorbing 112,000 calories per gram mole of carbon dioxide reacting, which is, as was said, the energy associated with an Einstein of light of wave length 2,300 Angstroms or less. Chlorophyll absorbing red light, which corresponds to energy of only 40,000 calories per Einstein, can perform work which would otherwise demand at least 112,000 calories per gram mole. This is a function performed by chlorophyll.

(3) Certain dyes when placed on photographic films (having light-sensitive coatings) enable the photographer to take pictures under what would otherwise be adverse conditions for the photochemical decomposition of the silver halide of the sensitive coating, and thus these dyes are said to sensitize the film.

*Requisites* : Investigation of radiation phenomena is dependent upon the availability of : (1) A continuous source of radiation furnishing the desired wave lengths ; (2) A means of focusing and dispersing this radiation into bands of definite wave lengths ; (3) A means of interposing a suitable sample ; (4) A means of detecting, measuring and recording the transmitted radiation.

The ultimate *source of radiation* is the atom or molecule of the substance. When radiation is emitted by a substance, energy is lost by its molecules and atoms ; and conversely when a substance absorbs radiation, energy is gained by its molecules and atoms. The more powerful the radiation the more profound the change in the molecule or atom. The following table contains a summary of the various types of radiation and the corresponding changes that result (see Nuclear Chemistry) :

Type of Radiation	Wave Length (Angstrom)	Result
Far infra-red ..	>200,000	Molecular spin
Near infra-red ..	>10,000	Atomic vibration in molecule
Visible and ultra-violet	1,000-8,000	Outer electron displacement in the atom
X-ray and gamma	About 1 A.U. or less	Displacement of electrons near the nucleus of atoms
Cosmic and radio-active	( $10^{10}$ calories per Einstein)	Transmutation of the nucleus of atoms

For *focusing and detecting* radiation the spectroscope is most commonly used (see Spectroscope). The construction of the lenses, prisms, and recording apparatus is determined by the particular portion of the radiation spectrum under investigation. The optical system must not absorb or alter in any way the wave length of the light under investigation. Each substance will either reflect, absorb, or transmit light in its own characteristic way. Thus, (1) glass is opaque to ultra-violet and infra-red radiation but transmits visible light ; (2) quartz is very transparent to ultra-violet and visible radiation, but opaque to

infra-red ; (3) salt crystals, especially sodium chloride and potassium bromide, are transparent to infra-red radiation.

The *detection and recording* of radiation is based upon the power to initiate the photochemical decomposition of silver halides on a sensitized photographic film. The primary reaction,  $\text{AgBr} + h\nu = \text{Ag} + \text{Br}$ , can be activated by radiation of short wave lengths such as blue, violet, ultra-violet, and X-ray, and furthermore where the proper sensitizer is present the reaction can be activated by the long wave lengths, such as red and infra-red. Because of the wide range of sensitivity of the photographic film to radiation it is one of the more common recording agents used with the spectroscope in studying the chemical and physical aspects of radiation.

Ultra-violet and infra-red spectroscopy are used in industry and research (1) to determine the structural constitution of compounds ; (2) to analyse compounds and mixtures ; (3) to obtain thermodynamic data.

In the field of analysis infra-red spectroscopy is the ideal tool for determining the composition of mixtures which are nearly similar in constitution and properties, for example : (1) When the full range of infra-red radiation strikes a benzene molecule every part of it is inclined to undergo diverse modes of orientation. These ring orientations give rise to bands which vary in position according to the degree and position of the substituent in the benzene ring. Thus monosubstituted benzenes give bands at 131,500 A.U. to 135,000 A.U. ; disubstituted benzenes at 120,800 A.U. to 135,000 A.U., with distinctive bands for ortho, meta, and para substitutions. (2) The determination of percentage of water in mixtures of acetone and water, even in the presence of other impurities, has been successfully worked out by means of infra-red spectroscopy (see *Ind. Chem.*, **24**, 647 (1948), Fig. 4). (3) Polymers and plastics.

In the field of heating infra-red radiation shows great promise, especially since the development of new materials that permit a high transmission of infra-red radiation. Illustrations are the solar heating of greenhouses and solariums ; medical diathermy ; and the fantastic possibility of obtaining heat and power from ice water (H. Barjot, "Extracting Heat and Power from Ice Water," *Power*, March, 1930).

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**LIGHT METALS** — Those metallic elements that have a specific gravity of 3 or less, the most important being aluminium, magnesium, and beryllium.

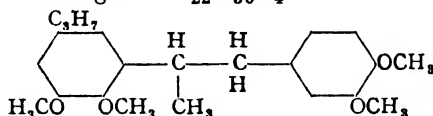
**LIGHT OILS** — The commercial hydrocarbon products from light oils, including various qualities of benzol, toluol, xylol, naphtha, etc., have been standardized, and specifications are issued by the B.S.I. (B.E.S.A.). (See Coal.)

**"LIGNASAN"** (Du Pont) — Trade-mark for a fungicide and bactericide containing ethyl mercury phosphate. Used for controlling blue stain on freshly sawed lumber, for the biological control of paper-mill slime, and for the preservation of starch and adhesives.

**LIGNIN** — Lignin is supposed to result from dehydrating changes in the cellulose forming the original walls of living wood cells, so that the heart of a tree is composed largely of lignin as distinct from the soft, pithy living parts; the major part being in combination with polysaccharides.

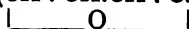
The free lignin can be extracted by alcohol and the combined lignin by resolving lignocellulose into its constituents by heating with 4 per cent. sodium hydroxide at 10 atmospheres pressure for one hour. This treatment is stated not to decompose the lignin, which can be precipitated by acidification and then extracted with alcohol.

According to W. J. Powell and H. Whittaker (*J.C.S.*, **127**, 132 (1925)), the lignins from the various natural sources are derivatives of the same hydroxy compound, differing only in the number of methoxy groups respectively contained. Aulin-Erdtman (1944) proposes the following formula for lignin:  $C_{22}H_{30}O_4$



Lignin can be obtained by the treatment of wood with 70 per cent. sulphuric acid, but a better result is said to be obtained by first of all saturating the powdered wood with a mixture of acetone and ethyl alcohol and treating the product with strong hydrochloric acid. The cellulose and other carbohydrates are dissolved and the lignin is left behind, amounting to some 28 to 30 per cent. of dry woods, representing the microscopic structure of the wood cells.

Lignin is said to be obtainable from straw by digestion with an alkaline carbonate, precipitation from the extract by acid, and purification by repeated solution in alkali and reprecipitation with acid. It is almost completely dissolved by digestion in 5 per cent. caustic soda solution at 170° C., and wood lignin is stated to yield protocatechuic acid by fusion with caustic potash, pyrocatechol being subsequently formed from it by elimination of carbon dioxide in presence of air. When prepared from pine wood by treatment with 45 per cent. hydrochloric acid and subsequently distilled, furfural (furfuraldehyde) (CH : CH.CH : C.CHO) is obtained.



In a study of the degradation products of lignin it has been shown that wood meal is converted almost quantitatively within a few days into products soluble in water by treatment with a mixture of acetic acid and acetic anhydride (1 : 1) containing 9 to 10 volumes of sulphuric acid. (See *The Proven Chemistry of Lignin*, by Brauns in TAPPI monograph, Series No. 6, 108-132 (1948).)

**LIGNITE** — A brownish-black natural deposit allied to coal, occurring in many parts of the world, including Bovey Tracey in Devonshire, and of which great deposits near the surface of the earth are found in Germany, Greece, Northern Ontario and other parts of Canada, North Dakota, Australia, New Zealand, India, Burma, and the Malay Peninsula, while deposits in Holland and Italy have been largely worked since 1917. They usually contain from about 20 to 50 per cent. water, from 27 to 43 per cent. of carbon, generally disintegrate upon drying, and will not coke. They yield so-called paraffin oil upon distillation, and their calorific value is about half that of coal. The transformation of lignite into petroleum and benzol is said to be effected by treating the powdered substance with hydrogen gas under a pressure of 100 atmospheres at about 200° C., 5 per cent. hydrogen being required to obtain petroleum, and 10 per cent. for producing benzol. When mixed with tar oil, lignite is stated to be hydrogenated by the "Bergius" process in two stages, first under pressure, and this is repeated in presence of a catalyst at 450° C., and subject to a pressure of 200 atmospheres, yielding 50 per cent. of motor fuel. (See Berginization.)

The lignite from the Riebeck Montan Works yields 15 per cent. of a quality of bitumen which is soluble in hot benzene and 8 per cent. of another quality which is dissolved at a higher temperature, a large part of the extractives being identical in composition with so-called Montan wax. The insoluble part yields the major portion in a soluble form on heating with alkali in solution as so-called "humic acids," which are precipitable upon acidification of the alkaline extract.

The waxy substance, forming 82.4 per cent. of the bitumen from Rhenish lignite, is stated to contain myricyl alcohol and another alcohol termed bituminol ( $C_{32}H_{66}O$  or  $C_{32}H_{64}O$ ) in the ratio 1 : 5, together with acids like those of central German lignites—viz., carboeric acid ( $C_{27}H_{54}O_2$ ) and montanic acid ( $C_{29}H_{58}O_2$ ) in ratio 1 : 1.

There is for each particular brown coal or lignite a temperature limit (usually between 300° and 400° C.) to which it may be heated, thus effecting a considerable chemical condensation in its cellulosic or humic constituents, steam and carbon dioxide being thus generated. This condensation constitutes a possible means of "up-grading" them, thus improving their fuel values.

Both brown coals and lignites are regarded by some as intermediate forms between peat and bituminous coals, while others think that brown coals have originated from vegetable debris different from that which in carboniferous times gave rise to our present bituminous coals. The pulverized form of lignites can be used under boilers for steam raising. (See Brown Coals, Coal, and Waxes (Montan).)

**LIGNOCERIC ACID** ( $C_{24}H_{48}O_2$ ) — A member of the normal fatty acids, melting at  $80^\circ C.$ , contained in many oils, including arachis oil.

**LIGNUM VITÆ** — See Guaiacum Wood.

**LIGROIN** — See Petroleum Ether.

**LIMA WOOD** — See Pernambuco.

**LIME** — Strictly interpreted lime is calcium oxide ("burnt lime") ( $CaO$ ), but is rather commonly used as applying to calcium compounds (see same). When expressing the composition of a calcium compound, for example, calcium carbonate, the percentage of lime means the *calculated* percentage of calcium oxide. "Slaked lime" or "hydrated lime" is calcium hydroxide ( $Ca(OH)_2$ ). "Lime water" is calcium hydroxide solution in water. "Limestone" is calcium carbonate ( $CaCO_3$ ).

**LIME (OIL OF)** — The essential oil obtained by expression from the rind of *Citrus limetta*, cultivated in Southern Europe. It contains from 6 to 10 per cent. of citral, with pinene, dipentene, and limonene; sp. gr. 0.872 to 0.885 at  $15^\circ C.$ ; opt. rot.  $+35^\circ$  to  $+40^\circ$ ; ref. ind. 1.476 to 1.485 at  $20^\circ C.$ ; soluble in alcohol and ether. It is used as a flavouring agent and in perfumery. West Indian oil of lime is obtained by expression or distillation from the rind of *Citrus medica* and resembles oil of lemon but is more intense in odour.

**LIME-SEED OIL** — The oil obtained from the pips (seeds) of *Citrus medica*, var. *acida*, as a by-product in the citrus industry, amounting in all to some 39.8 per cent.; greenish-yellow to light brown in colour, sp. gr. 0.924, acid v. 13.6, sap. v. 197.7, i.v. (Hübl) 109.5, and ref. ind. 1.4635 at  $40^\circ C.$  There are several varieties, and in general it resembles cotton-seed oil, and might be used in soap-making, but presents difficulties in refining for edible use. The meal has a high manurial value and good feeding value. A. E. Collens gives the following values in respect of a sample of clarified oil: Sp. gr. at  $27^\circ/15.5^\circ C.$ , 0.9138 solidifying point,  $-3^\circ C.$ ; ref. ind., 1.4740 at  $28^\circ C.$ ; acid v., 11.2 sap. v., 193.5; i.v., 109.7 (Hübl); soluble in alcohol 0.18 per cent. unsap. matter 0.72 per cent.

**LIME-SODA PROCESS** — See Sodium (Hydroxide).

**LIMESTONE** — See Calcium (Carbonate).

**LIMONENE (Dextro-Limonene)** ( $C_{10}H_{16}$ ) — The oil of orange rind consists almost entirely of this terpene, which is also a constituent of carvene, dill oil, and citron oil. It is a monocyclodiolefin hydrocarbon, boiling at  $177^\circ C.$ , and of sp. gr. 0.842.

**Lævo-Limonene** is present to some extent in the oil of fir-cones, associated with other terpenes.

**Dipentene** is inactive limonene. (See Dipentene, and Orange Oil.)

**LIMONITE** ( $2Fe_2O_3 \cdot 3H_2O$ ) — See Iron.

**LIMPID** — Characteristic of clear and transparent fluids.

**LINALOE OIL** — A Mexican distilled wood-oil from *Bursera delpechiana* and *B. aloexylon* to extent of about 3 per cent. ; colourless, fragrant, containing linalool and geraniol, of sp. gr. from 0.875 to 0.890, soluble in alcohol and ether, and used in perfumery.

**LINALOOL (Coriandrol, Linalol)** ( $C_{10}H_{18}O$ ) — A liquid of sp. gr. 0.868 and b.p.  $198^{\circ}C.$ , contained in linaloe oil, and isomeric with geraniol and nerol ; occurring as linalyl acetate ( $C_{10}H_{17}OOC.CH_3$ ) in the cacao-bean and the oils of bergamot, lavender, coriander, neroli, and sage. It is soluble in alcohol and ether, and used in perfumery. Linalyl acetate can be made by the action of acetic acid on linalool in presence of sulphuric acid ; it has sp. gr. of 0.895, boils at  $220^{\circ}C.$ , and is used in perfumery. (See Linaloe Oil.)

**LINARITE** — A crystalline, mineral, basic, copper-lead sulphate ( $PbSO_4, CuH_2O_2$ ) (crystal system No. 5, and sp. gr. 5.3 to 5.45).

**LINDEN OIL** — See Basswood Oil.

**LINEN** — Thread or cloth manufactured from the fibres of the flax stem. Linen yarn is stated to usually contain about 25 per cent. of impurities, which are more or less removed in the bleaching processes effected by means of hypochlorites after scouring with an alkaline solution. Physical tests such as those affecting strength, extension, stiffness, rigidity of linen materials depend largely upon the moisture content. (See Flax.)

**LINOLEIC ACID (Linolic Acid)** ( $C_{17}H_{31}.COOH$ ) occurs as a glyceride in linseed, poppy, hempseed, and other drying oils, and as a smaller constituent of some non-drying oils. When pure it is a water-white oily liquid which remains fluid at  $-18^{\circ}C.$  and has a b.p. of  $229^{\circ}$  to  $230^{\circ}C.$  under 16 mm. pressure. A sample of this acid prepared from poppy-seed oil has been reported to have i.v. (Hanus) 178.6, acid v. 196.7, sp. gr. at  $20^{\circ}/4^{\circ}C.$  0.9025, and m.p.  $-25^{\circ}$  to  $24^{\circ}C.$  (See Linseed Oil.)

**LINOLENIC ACID** ( $C_{17}H_{29}.COOH$ ) — Occurs as a glyceride in linseed, hempseed, and some other drying oils, and is very oxidizable. It is nearly colourless, of fishy odour ; sp. gr. 0.923 ; soluble in alcohol and ether, and furnishes a zinc compound ( $C_{18}H_{29}O_2$ ) $_2Zn, \frac{1}{2}ZnO$ , m.p.  $72^{\circ}$  to  $73^{\circ}C.$  (See Elæostearic Acids, and Linseed Oil.)

**LINOLEUM** — Linoleums are made by coating a suitable fabric such as canvas with mixtures of raw and boiled linseed oil and impregnating or coating with mixtures of "linoleum cement," powdered cork, and the desired pigments, by hot rolling. The linoleum cement is a mixture of boiled linseed oil, gums or resins, cork-dust, pigment, and other filling materials.

**LINOXYN** — See Linseed Oil.

**LINSEED OIL** is expressed by pressure from ground flax seed (*Linum usitatissimum*), supplies coming from Argentina, British India, the U.S.A., and Canada.

Linseed yields by pressure alone from 18 to 20 per cent. ("cold drawn"), but when aided with heat, about 27 per cent. of oil, and by total extraction up to 38 per cent. on average; it contains about 7 to 9 per cent. water, 19 to 22 per cent. albuminoids, 19 to 23 per cent. digestible carbohydrates, 5 to 8 per cent. woody fibre, and 4 to 5 per cent. mineral matter. The oil is largely used in making paints, varnishes, printing inks, linoleum, patent-leather lacquers, rubber substitutes, and soft soaps, also for treatment of scalds and burns, while the residual cake is used for feeding cattle. The cake contains hydrocyanic acid derived from a contained glucoside, but most of it is dissipated during the maceration of the seeds and by evaporation. On average the cake as imperfectly pressed contains 10 to 11 per cent. water, 7 to 11 per cent. oil, 30 per cent. albuminoids, 6 to 10 per cent. woody fibre, and 6 to 7 per cent. mineral matter.

The oil solidifies at  $-27^{\circ}\text{C}.$ , has a sp. gr. at  $20^{\circ}\text{C}.$  of 0.927 to 0.932, sap. v. 188 to 195, i.v. (Hübl-Waller) 170 to 192, and ref. ind. 1.4725 at  $15^{\circ}\text{C}.$  During drying, the ref. ind. of a film rises to 1.50 and upwards. It contains 85 to 90 per cent. liquid glycerides—namely, about 5 per cent. oleic, about 80 per cent. linoleic and linolenic, the rest being glycerides of solid fatty acids, chiefly palmitic. It is typical of the class of "drying oils," so called from their readiness to absorb oxygen upon exposure to the air, being changed thereby into a transparent, sticky mass. Linseed oil by absorption of oxygen forms the substance known as **linoxyn** (a complex mixture of oxidized glycerides), which is insoluble in ether, and reported to be capable of absorbing 15 per cent. of its weight of water.

When first expressed, the oil is pale yellow and not disagreeable in smell, but unless refined by treatment with a small percentage of either sulphuric acid or alkali, it quickly turns rancid, dark, and repulsive in odour. It is soluble in alcohol, chloroform, carbon disulphide, benzol, and turpentine. Heating alone, under pressure, at a constant temperature greatly increases its viscosity and the iodine value decreases, while polymerized linseed oil, resulting from the action of heat, is stated to have a sap. v. of 206. A brighter, clearer "stand" oil can be more economically produced by submerged combustion of linseed oil, using the "Hammond" burner directly submerged in oil. Upon boiling (which begins quietly at about  $260^{\circ}\text{C}.$ ) until it loses one-eighth of its weight, it thickens, becomes viscid, and dries quickly upon exposure to air. The mucilage contained in raw linseed oil "breaks down" when the oil is heated to about  $250^{\circ}$  to  $260^{\circ}\text{C}.$ , and after this has occurred, it is possible to clarify and dehydrate the oil by means of super-centrifugal force, thus producing a product practically equal to boiled oil which has been tanked for twelve months. The oxidation of linseed and rape-seed oils by a current of air is facilitated by the use of a little manganese dioxide or other drier, and this process enriches them with hydroxy acids, tri-glycerides deepening their colour, and giving "body" and drying properties to the product. The setting or drying of linseed oil is accelerated by the presence of such gels as size and glue, and is attributed to a wetting process induced by their

presence. The bleaching of linseed oil by action of sunlight in glass-covered pots for a period of from three to six weeks is said to give a superior product, but it requires to be subsequently washed to free it from traces of acid, etc. Saponified with alkalis, linseed oil gives soft soap of a thin character. Both the ground linseed and the residual oil cake are used in making poultices. Linseed oil is to a small extent used in medicine, sometimes internally, but the boiled varieties are unsuitable for these purposes, owing to the manganese or lead that they may contain. It is no longer used, as formerly, in the form of carron oil for the treatment of burns.

*References* : "Composition of Linseed Oil," by N. E. Cocchinaras (*Analyst*, **57**, 233 (1932)); "Rate of Linseed Oil Oxidation with Driers," by A. J. Currier and I. H. Kagarise (*Ind. Eng. Chem.*, **29**, 467 (1937)); "Drying of Linseed Oil"—Electron diffraction study D. H. Clewell (*Ind. Eng. Chem.*, **29**, 650 (1937)); Paints, and Varnishes.

**LINTNER VALUE** — Diastatic value or measure of the hydrolytic change of starch to maltose under stated conditions. (See Ministry of Agriculture and Fisheries, Statutory Rules and Orders, 1929, No. 1115; H.M. Stationery Office.)

**LIPASE** — See Enzymes.

**LIPOIDS (LIPINS)** — Terms loosely applied to various naturally occurring substances of an oily nature, such as glycerides, lecithins, phosphatides, and even sterols, but the names, if used at all, should be reserved for those substances the molecules of which contain fatty-acid residues.

**LIQUATION** — The stage reached, when heating an ore or other metallic mixture containing ingredients differing sensibly in fusibility, at which the most fusible constituent melts and flows away from the mass. The term has a somewhat special meaning in respect of alloys, which, when melted, sometimes separate more or less in layers of their several components.

**LIQUIDAMBER (Storax)** — See Balsams.

**LIQUID FUEL** — See Brown Coals, Fuel (Liquid), Motor Spirit, Petroleum, and "Synthol."

**LIQUIDS and LIQUEFACTION** — See Matter.

**LIQUID SPREADING** — See Capillary Attraction.

**LIQUORICE** — The dried peeled or unpeeled root and stolon of *Glycyrrhiza glabra* and other species of *Glycyrrhiza*, a shrub widely distributed in Southern Europe and exported chiefly from Sicily, Spain, and Syria. By extraction with hot water and evaporation, it yields an extract (Liquorice Juice) which contains from 12 to 16 per cent. of glycyrrhizin, a sweet amorphous substance. Glycyrrhizin possesses about 50 times the sweetening power of sucrose and consists of the calcium and potassium salts of glycyrrhizinic acid; on boiling with dilute sulphuric acid, it yields dextrose and it has been ascribed the molecular formula,  $C_{30}H_{48}O_{13}$ . According to A. Giammona fresh liquorice

extract contains 1.38 per cent. dextrose and 3.18 per cent. sucrose, and the same root, after air drying and storing for three months, yields an extract containing 2.37 per cent. of dextrose and 5.40 per cent. sucrose. Commercial liquorice extracts, produced in Sicily, normally contain about 8 per cent. of reducing sugars and about 8 per cent. of non-reducing sugars.

Liquorice extract is used in tobacco products to convey moisture conditioning and flavour. It is used also in pharmaceutical products and confectionery. Spent liquorice root is used in the production of insulation board, boxwood, and other fibre products. (See "Liquorice, Putting a Weed to Work," Streatfield Memorial Lecture, by P. A. Houseman, Royal Institute of Chemistry, London, 1944.)

**LITER** — See Weights and Measures.

**LITERATURE (Chemical)** — See Chemical Literature.

**LITHARGE (Lead Monoxide)** — See Lead (Oxides).

**LITHIUM (Li) and its Compounds** — Atomic weight, 6.940. See Elements for other data. Lithium is a somewhat rare element found in small quantities, but widely distributed in nature, in association with certain minerals including *petalite*, *spodumene*, and *lepidolite* (*lithium mica*), deposits of which occur in Manitoba and West Ontario (Canada), the U.S.A., Sweden, France, Spain, Saxony, Bohemia, etc., all of which are, in the main, silicates of aluminium. Large deposits of lithium ore occur also in Namaqualand and the Karabib district of S.W. Africa. It also occurs in the forms of *amblygonite* ( $\text{LiAlFPO}_4$ ) (a fluophosphate found in California, South Dakota, Saxony, and Bohemia, etc.); *montebrasite* (both with an average lithium content of about 9 per cent.), associated with *cryolite* ( $\text{Na}_3\text{AlF}_6$ ) in Greenland; and in several mineral waters which are extensively used for medicinal purposes. Lepidolite is employed in the making of certain varieties of glass owing to its high fluorine content. Approximately 10,000 tons per year of lithium minerals is produced in the U.S.A., and 1,000 in South West Africa.

Metallic lithium is the lightest metal known, with a specific gravity of 0.534. It is silvery white, softer than lead and tarnishes quickly when exposed to air. It must be kept in air-tight containers, or under naphtha or kerosene. It is produced commercially by the electrolysis of the fused chloride. See "Lithium, Theoretical Studies and Practical Applications," by H. Osborg (*Trans. Electrochem. Soc.*, **66**, 91 (1934)). Some attention has also been given to its preparation by vacuum metallurgy, an account of which is contained in a paper by W. J. Kroll and A. W. Schlecten (*Metals Technology*, **14**, T.P. 2179 (June, 1947), and *Metals Industry*, **70**, 395 (1947)).

The metal has been put to many uses in the ferrous and non-ferrous industries as a refining, degasifying, and deoxidizing agent, and as an alloying agent. When added to lead it imparts outstanding properties to the alloy which makes it suitable for railroad bearings and journals; added to copper, it improves the conductivity and metal soundness; and, added to magnesium, it produces better cold formability and lower density. The use of lithium atmosphere for the heat treating

of steels without scaling is another wide application for the metal. (See R. S. Burpo, Jr., *Materials and Methods*, **24**, 622 (Sept. 1946)).

When heated in hydrogen gas, **lithium hydride** is formed, and this product, when subjected to electrolysis, gives off hydrogen at the anode—the first known instance of that element functioning as a negatively charged ion. Lithium hydride is stable upon heating, but is decomposed in strong sunlight. With water lithium hydride evolves hydrogen gas, and this is used as a portable source of the gas. It also combines with nitrogen of the air at ordinary temperatures, forming **lithium nitride** ( $\text{Li}_3\text{N}$ ).

**Lithium oxide** (**Lithia**) ( $\text{Li}_2\text{O}$ ) exhibits alkaline properties, and in common with the carbonate is used medicinally as an antidote to gouty complaints by removal of uric acid.

Among the best-known lithium compounds are the **hydroxide** ( $\text{LiOH}$ ), the **carbonate** ( $\text{Li}_2\text{CO}_3$ ) (only slightly soluble in water), the **chloride** ( $\text{LiCl}$ ), and the **phosphate** ( $\text{Li}_3\text{PO}_4$ ).

The hydroxide is used in the construction of certain electrical storage batteries, while the chloride, bromide, citrate, and iodide are all soluble in water and used in medicine. Lithium chloride solution has been proposed (*Ind. Eng. Chem.*, **27**, 879 (1935)) as a means of obtaining air of low humidity, to as low as 11 per cent. water vapour, for use in air-conditioning. The carbonate, citrate, and iodide are also used in compounding mineral waters, whilst the fluophosphate and the fluoride are used in ceramics and enamels, as also lepidolite.

The volatile lithium salts, especially the chloride, give a crimson tinge to flame.

**LITHOPONE** — See Paints.

**LITMUS** — A violet-blue colouring matter used as an indicator, prepared from the lichens *Lecanora tartarea* and *Rocella tinctoria* by treatment with ammonia and potash, and then fermenting, after which alum, potash, and lime are added, and when the maximum colour is attained, sand and chalk are incorporated to give solidity to the mass preparatory to drying. Litmus paper is absorbent filter or blotting paper stained by soaking in a solution of litmus and subsequently drying. Acid solutions turn this blue to red, and alkaline solutions restore the blue colour, so it is commonly used to determine the alkaline or acid nature of liquids. Litmus paper can be prepared of a neutral tint that is equally amenable to both reactions. Litmus solution may be used for the same purposes as litmus paper. (See Volumetric Analyses.)

**LITRE** — See Weights and Measures.

**LIVER OF SULPHUR** — An old name still used commercially in respect of a mixture of potassium polysulphides as prepared by heating one part by weight of sulphur and three parts of potassium carbonate. Used as an insecticide and fungicide.

**LIXIVIATION** — The extraction by solution of soluble substances from materials containing them, such as *black ash*, that is, crude sodium carbonate, as made by the old Leblanc process. (See Extraction, Leaching, and Sodium (Carbonate).)

**LOADSTONE (Lodestone)** — See Iron.

**LOAM** — Clay more or less mixed with sand or marl.

**LOBELINE (Lobelanine)** — An alkaloid isolated from the lobelia plant, *Lobelia inflata*, which is cultivated in the eastern parts of the U.S.A. It is stated to have the molecular formula  $C_{22}H_{27}O_2N$ . It is used in medicine, in the form of its hydrochloride, as a respiratory stimulant in childbirth, and for coal-gas poisoning. The alkaloidal content of lobelia is described by Toman in *Amer. J. Surg.*, **60**, 270 (1943).

**LOCUST-KERNEL (GUM AND OIL)** — Prepared from the endosperm of the locust or carob bean (*Ceratonia siliqua*).

**LODE** — A vein or fissure in rocks filled with metalliferous deposit.

**LODGE-COTTRELL PROCESS** — See Cottrell Precipitating Plant.

**LOGWOOD EXTRACT (Hematine)** — An aqueous extract of the heart-wood of *Hæmatoxylon campechianum* (Fam. Leguminosæ), a tree which grows in Mexico, Central America, and the West Indies. It contains about 50 per cent. of hæmatoxylin ( $C_{16}H_{14}O_6 \cdot 3H_2O$ ), which, when pure, is a colourless crystalline substance acquiring a reddish colour on exposure to air. Hæmatoxylin is sparingly soluble in water, but dissolves in aqueous solutions of alkalis to give a purple colour. Logwood extract is used in making ink and has been used as a dye.

“**LORO**” (Du Pont) — Trade-mark for an insecticide containing chiefly lauryl thiocyanate. Used as a contact insecticide for controlling red spider, mealy bugs, chrysanthemum midge, thrips, and aphids.

“**LOROL**” (Du Pont) — Trade-mark for a mixture of normal primary fatty alcohols, principally lauryl alcohol. Used as an anti-foam agent, a spectral lubricant, a plasticizer, and a chemical raw material.

**LOW-TEMPERATURE CARBONIZATION** — See Coal.

**LOW TEMPERATURE RESEARCH** — See lecture by W. Hardy in *Chem. and Ind.*, **52**, 45 (1933); “The Cryogenic Laboratory at Leiden,” by Robert Guillien in *Ann. Rep. of Smithsonian Institution*, 1936, 171 (Supt. of Documents, Washington); Heat, and Helium.

**LUBRICANTS AND LUBRICATION** — Lubricants are used to decrease the friction between opposed solid faces, which arises, as is supposed by some, from true cohesion (mutual attraction). By others, it is said that in a good lubricant an enormous army of molecules is held together by electrical forces without there being any chemical change.

The solid lubricants include natural and artificial graphite, talc, mica, metallic soaps, and other substances, such as “flowers of sulphur” and white-lead, which are used for curing hot bearings, but of course they vary according to the application to be made of them. The natural graphite is usually of the so-called flake variety, and varies in sizes of particles from  $\frac{1}{16}$  in. to less than  $\frac{1}{200}$  in., whilst the artificially produced kind is amorphous, and even finer. A preparation of the latter is sold under the trade names of “Aquadag” (which when air-dried contains about 62 per cent. carbon), “Hydrosol” (when in

admixture with water), and as "Oildag," "Oleosol," and "Kollag" (when in admixture with oil). (See Perkin Medal Address by E. G. Acheson (*J.S.C.I.*, 29, 244 (1910)).)

"Aquadag" used as a cylinder lubricant has been found advantageous where solid friction occurs, as in worm-gear, although equally good results have been obtained by the use of natural flake graphite; and it has been concluded that the highest lubricating value of graphite depends upon its chemical purity.

Generally speaking, solid lubricants are applied dry in cases where for special reasons it is inadvisable or not possible to use liquid or semi-solid lubricants, otherwise they are usually employed in admixture with oil or as ingredients in greases.

It has been represented that there are two distinct conditions concerning lubrication, namely, one in which the solid surfaces are separated by a film of liquid oil, the friction depending upon the viscosity of the lubricant; and another in which no such oil-film can form, so that the surfaces are in closer contact, and the efficiency of the lubricant then depends upon the "oiliness" and not upon the viscosity of the agent.

A method of determining the lubricating power of oils is by means of a machine which indicates the increase of temperature in a bearing rotated at a constant number of revolutions per minute.

It is required in a liquid lubricant that it shall penetrate into the narrow spaces between journal and bearing, thus "wetting" or spreading over the surfaces which are in motion together. The function of a lubricant is to keep metal surfaces separate with a minimum expenditure of energy. Vegetable and animal oils generally possess greater value than mineral oils obtained from crude petroleum and coal tar, which are also used as lubricants in common with the so-called rosin oil obtained by the destructive distillation of rosin. They are generally graded in accordance with their specific gravities and viscosities. (See Viscosity.)

The so-called "germ process" of lubrication employs one or more fatty acids with mineral oil as the instrument of lubrication, 1 or 2 per cent. being incorporated according to chemical circumstances. This is said to reduce the coefficient of friction from 0.0084 to 0.0052—that is, some 25 per cent. on a friction-testing machine.

Mineral lubricating oils contain only a small percentage of paraffin hydrocarbons of the  $C_n H_{2n+2}$  series, and consist chiefly of those which range from  $C_n H_{2n}$  to  $C_n H_{2n-8}$ . In oil refining, care should be taken not to destroy the more stable unsaturated hydrocarbons to which the viscosity of the oil is largely due, it having been shown that an increase in viscosity occurs concurrently with a decrease in the hydrogen content. The saturated compounds are principally cycloparaffinic (naphthenic, hydroaromatic), and these, as also the solid resinous components containing oxygen, are probably causes of "gumming," and their removal, together with the more oxidizable unsaturated hydrocarbons naturally reduces the "gumming" tendency.

Langmuir regards "polarity or unsaturated chemical affinity as an

essential factor for the production and maintenance of a boundary film." Experiments with cycloparaffin hydrocarbons appear to show that there is a linear relationship between lubrication and molecular weight; the greater the latter, the more efficient is the lubricant (W. F. Seyer and S. R. MacDougall).

The de-waxing of petroleum lubricating stocks is done by refrigerating the oil so as to throw the wax out of solution, naphtha being employed to dilute the stock if desirable and centrifugal force to complete the separation. (See Petroleum.)

The viscosity varies with the temperature; the hotter the oil the lower is its viscosity, and conversely the colder it is, the thicker it becomes. Oils exhibit a rapid increase in viscosity with pressure, this increase being much greater for the mineral than for animal and vegetable oils.

The essential tests for valuation of lubricants are specific gravity, viscosity, viscosity index, cold test, flash-point, coke test, and appearance. The viscosity index expresses the rate at which the viscosity of an oil changes with temperature, and the higher the viscosity index the lower the rate at which the viscosity *decreases* with increase of temperature. The standard oil of 100-viscosity index has Saybolt Universal Viscosity (S.U.V.) of 426 seconds at 100° F. and of 60 seconds at 210° F.; and the standard oil of low viscosity index, taken as 0, has S.U.V. of 781 seconds at 100° F. and of 60 seconds at 210° F. 781—S.U.V. of unknown at 100° F.

$\frac{781-426}{781-426} \times 100 = \text{Viscosity index of un-}$

known having S.U.V. of 60 seconds at 210° F.

An old lubricant for stopcocks, known as Travers', consisted of a mixture of rubber, "Vaseline," and paraffin wax, and an improved one has been described by E. G. R. Ardagh and A. L. Davison, made from pale crêpe rubber 7.5 per cent., white petroleum "Vaseline" 77.5 per cent., and paraffin wax of m.p. 128° to 130° F. 15 per cent. The "Vaseline" and wax are first melted together, and the rubber cut into small bits gradually added, keeping the mixture in motion at 130° C. for some six hours, after which it is allowed to set into an unctuous mass.

*References:* *Lubrication and Lubricants*, by L. Archbutt and R. M. Decley (Griffin and Co., London); *The Principles and Practice of Lubrication*, by Nash and Bowen (Chapman and Hall, London); *Theory of Film Lubrication*, by R. O. Boswall (Longmans, Green and Co., London); *Modern Methods of Refining Lubricating Oils*, by V. A. Kalichevsky (Reinhold Publishing Corp., New York); Cutting Fluids, Interfacial Tension, Soaps (Metallic), and "Voltol" Oils.

**LUCERNE** (*Medicago sativa*) — A leguminous plant, useful as a green food for cattle, largely grown in North and South America, and known in Spanish lands as *alfalfa*. When carefully cured in the dark, alfalfa is reported to be rich in vitamin A, and the juice of the plant is stated to contain the base adenine (6-aminopurine). (See Alfalfa, and Esparto Grass.)

**" LUCITE "** (Du Pont) — Trade-mark for a synthetic thermoplastic based on polymerized methyl methacrylate resin. It possesses notable clarity, weather resistance, low moisture absorption, shatter resistance, transmission of light, dimensional stability, and freedom from odour and taste.

**LUMBANG OIL** — See Candle-nut Oil.

**" LUMINAL "** — See Phenobarbitone.

**LUMINOSITY** — See Flame, Light, Phosphorescence, Radium, and Zinc (Sulphide).

**LUMINOUS PAINT** — See Calcium (Sulphide, and Tungstate), Paints, and Radium.

**LUNAR CAUSTIC** — Fused silver nitrate.

**LUPIN ALKALOIDS** — Contained in various species of lupins (*L. luteus*, *L. niger*, *L. albus*, *L. angustifolius*, and *L. polyphyllus*), including lupinine ( $C_{10}H_{19}ON$ ), sparteine ( $C_{15}H_{26}N_2$ ), and another body named lupinane, to which the formula  $C_{10}H_{19}N$  (b.p.  $82^\circ$  to  $83^\circ$  C.) has been assigned.

Lupinine is described as a white, crystalline, poisonous body, of m.p.  $68^\circ$  to  $69^\circ$  C., soluble in alcohol and ether, but decomposed by water.

**LUPULIN** — See Hops.

**LUTECIUM** — See Lutetium.

**LUTES** — Cements of refractory or other materials used to pack, seal, or repair the joints of manufacturing plant, varying in nature according to the chemicals concerned. Among these are litharge-glycerine cements, which resist the action of strong mineral acids and ammonia in a high degree, but are not stable against caustic alkalis and strong acetic acid. One good mixture recommended is 50 grams litharge and 60 c.c. of a mixture of 5 parts glycerine and 2 parts water; this hardens in ten minutes, and after three hours becomes very hard. Water is said to be a product of the reaction, which has been represented as  $3PbO + 2C_3H_5(OH)_3 = Pb_3(C_3H_5O_3)_2 + 3H_2O$ .

Hart's Indiarubber Cement is made from 12 parts raw linseed oil heated together with 12 parts masticated rubber worked up into a stiff paste with " paper stock " asbestos. It is a good cement for caulking glass pipes, such as those used for conveying hydrochloric acid gas.

Other materials employed include clay, pitch, tar, putty, linseed meal, bitumen, Portland cement, asbestos mixtures, etc. A cement for fixing iron in stonework is referred to under Ammonium Chloride. An acid-proof composition is made by melting together 30 to 40 parts sulphur with 60 to 70 parts of sand, and raising the temperature to  $150^\circ$  C., in which pasty state it is used as a plaster. Another cement that is recommended for water-proof joints is: 1 volume of litharge, 1 volume of fine sand, 1 volume of plaster of Paris, one-third volume of rosin powder, all to be mixed dry, and then boiled linseed oil and turpentine to be worked in until the mass is of the consistency of putty.

(See "Cements and Putties for Chemical Equipment," by A. G. Wright (*Chemical Industries*, **42**, 668 (1938)); "Caulking Compounds," by C. F. Mason (*Chemical Industries*, **42**, 421 (1938)); Cements; "Prodorite"; and Magnesia.)

**LUTETIUM (Lu)** — Atomic weight, 174.99. See Elements for other data. Lutetium is one of the rare-earth elements and belongs to the yttrium group of the same. The spelling lutetium was accepted (1949) by the International Union of Chemistry, former spelling lutecium.

**LYCOPodium** — Spores of *Lycopodium clavatum* used in medicine as a dusting powder and as a covering for pills. Consists of the spores themselves, a fixed oil, and sucrose. It is also used in explosives and pyrotechnics. The name is sometimes applied to the oil.

**LYDDITE** — See Explosives (Picric Acid).

**LYE (Ley)** — A solution of alkali such as used in soap-making.

**LYMPH** — Transuded serum of blood which has been reabsorbed from the tissues and carried back to the circulation by the lymphatics. It is alkaline, contains about 5 per cent. solid constituents made up of plasma and white corpuscles, and is really diluted blood-serum, from which the tissues have taken up what they require for nourishment.

"**LYSOL**" — A registered trade mark for a disinfectant and antiseptic containing essentially soap, cresylic acid, and *ortho*-hydroxydiphenyl. It forms clear solutions with water in all proportions.

*m* — Meta (see Meta Compounds).

**MACASSAR OIL** is obtained from the seeds of *Schleichera trijuga* (India, Malaya, and East Indian Archipelago). The fat from the seeds extracted by ether or carbon tetrachloride is yellowish-white, of pleasant odour, has a sp. gr. at 99°/15° C. of 0.86, m.p. 21° C., sap. v. 214.4 to 229.1, and i.v. 52.4 to 55. It is used for burning purposes, in soap-making, as an edible oil, in medicine, and in cosmetics.

**MACE** — The dried arillus of the nutmeg, obtained from the fruit of *Myristica fragrans*, a tree cultivated in the Molucca Islands, India, and the East Indies. It contains from 4 to 15 per cent. of volatile oil and is used as a condiment and in making sauces and pickles. (See Mace Oil, and Nutmeg.)

**MACE OIL** — The volatile oil obtained by distillation from the arillus of the nutmeg. It is a colourless or slightly yellow oil of aromatic odour, containing camphene, terpineol, and dipentene. It is indistinguishable from oil of nutmeg, and is used in perfumery and as a flavouring agent. (See Nutmeg.)

**MACROCHEMISTRY** — Methods of chemical examination of quantities *en masse*, as contrasted with atomic or molecular amounts, and as distinguished from microchemistry. (See Microchemistry.)

**MADDER (Turkey Red)** — The powdered root of various species of *Rubia*, especially *R. tinctorium* (Fam. Stellatæ), an herbaceous perennial cultivated in Alsace, France, the Levant, and Holland. It contains the glycoside ruberythric acid, which on hydrolysis yields xylose, glucose, and alizarin, the beautiful red dye. (See Alizarin, and Purpurin.)

**MAFURRA SEED OIL (Mafoura)** — From Portuguese East Africa ; is yielded to the extent of 33 to 60 per cent., and reported to have an i.v. of 46 to 47·5. (See Mafurra Tallow.)

**MAFURRA (MAFOURA) TALLOW** — A product of the nuts of *Trichilia emetica* from Portuguese East Africa ; being a solid fat obtained from the husk and kernel, and different from the oil obtained from the aril ; sap. v. 202·5, i.v. 66, m.p. from 35° to 45° C.

**MAGADI SODA** — See Trona.

**MAGENTA or FUCHSINE** — The monohydrochloride of rosaniline, a triphenylmethane dyestuff prepared by the oxidation of a mixture of equimolecular amounts of aniline, *p*-toluidine, and *o*-toluidine with nitrobenzene in the presence of iron. It dyes silk and wool directly but for cotton requires a mordant. (See Rosanilines, and Triphenylmethane.)

**MAGISTRAL** — A crude mixture of cupric and ferric sulphates and oxides, prepared by roasting pyrite, and used in the Mexican amalgamation silver extraction process. (See Silver.)

**MAGMA** — A paste of finely divided material.

**MAGNESIA** — See Magnesium (Oxide).

**MAGNESITE** — See Magnesium.

**MAGNESIUM (Mg) and its Compounds** — Atomic weight, 24·32. See Elements for other data. Magnesium is found only combined in nature, abundantly in combination with calcium as a double carbonate in the form of the mineral *dolomite*, containing variable proportions of the two substances ; also in *magnesite* and *brucite*, and as silicates in *serpentine* and *talca*. Magnesium compounds are found in brines and ocean water (0·01 pound per gallon). See "Magnesium Compounds from Ocean Water," by H. H. Chesney (*Ind. Eng. Chem.*, **28**, 383 (1936)).

*Magnesite*, or *Greekstone*, is essentially magnesium carbonate ( $\text{MgCO}_3$ ), crystal system No. 3, and sp. gr. 3·0, and in some forms is nearly pure, large deposits occurring in Canada, Eastern Washington (U.S.A.), Venezuela, Greece, Austria, Hungary, India, Manchuria, Russia, and other countries, and is extensively used for making refractory bricks. These are made by grinding the magnesite as fine as possible, and made into bricks before kilning slowly to 600° C. for twenty-four hours, after which the temperature is raised to 1,650° C. for seventy-two hours. The calcined material is then ground with sufficient water to make a pasty mass until 95 per cent. passes through a sieve of thirty meshes to the linear inch, after which the material is again moulded into bricks, dried for some seven days, and then kiln-fired at 1,650° C.

for seven days (G. H. Read). Articles of fused magnesite such as crucibles are now also produced, the sp. gr. of the fused material, which is of a milky amber colour, being 3.5 to 3.62. An article on Canadian magnesite by F. E. Lathe is reproduced in the *C.T.J.*, **86**, 156 (1930). *Brucite* is a native form of magnesium hydroxide ( $\text{Mg}(\text{OH})_2$ ) found in serpentine rocks in Shetland and Texas. *Periclase* is a native oxide of magnesium ( $\text{MgO}$ ), and *spinelle* is a natural crystalline magnesium aluminate. *Kieserite* is magnesium sulphate ( $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ ), and *carnallite* (one of the Stassfurt salts) is a double chloride of magnesium and potassium ( $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ).

Metallic magnesium is produced commercially by three processes, *i.e.*, the electrolytic, silicothermic (Pidgeon), and the carbothermic (Hansgrig). The electrolytic process depends on the reduction of fused anhydrous magnesium chloride, derived from either sea water, brine wells, or converted ores such as dolomite, magnesite, and carnallite. The other two processes depend on the thermal reduction of magnesium oxide from dolomite or magnesite. The Pidgeon process, known for its lowest capital investment, employs a high-temperature reaction in an evacuated steel retort using ferrosilicon as the reducing agent. Other agents such as aluminium, aluminium-silicon, and calcium carbide may also be substituted for the ferrosilicon but they are not as satisfactory. In the Hansgrig process the oxide and carbon react at very high temperature under ordinary pressure, and the products are shock quenched by a blast of hydrogen or natural gas. A comprehensive account of these processes is contained in the book *Magnesium-Extraction Metallurgy*, by L. M. Pidgeon (American Society for Metals, Cleveland, Ohio).

Magnesium is a silvery-white metal which tarnishes slightly upon long exposure to air. It is regarded as an inexhaustible metal, for estimates claim that about 4,500,000 tons of magnesium may be extracted from one cubic mile of ocean water. In fact, all the magnesium so far produced could have been obtained from one-tenth of a cubic mile of ocean water. Magnesium has long been used for flash lights in photography, and in pyrotechnics, and for this reason the metal has been regarded as highly inflammable when heated. This fact holds only for very fine metallic dust but not for massive magnesium alloys or parts. Positive proof that burning of magnesium and its alloys necessitates melting in air has been presented by L. A. Carapella and W. E. Shaw (*Metals and Alloys*, **22**, 415 (1945)). These alloys are good conductors of heat and have relatively high melting points. The applications for these alloys are rapidly growing and it is believed that magnesium will become an outstanding non-ferrous material for industrial uses.

Magnesium forms alloys with many metals. (See "Fundamental Alloying Nature of Magnesium," by L. A. Carapella (*Metal Progress*, **48**, 297 (1945)).) Alloys of commercial importance are those containing aluminium, cadmium, cerium, manganese, tin, zinc, and zirconium. These alloys are readily cast and easily fabricated into many wrought shapes and forms. Magnesium alloys are the lightest

structural materials and possess an outstanding strength-weight ratio and an unsurpassed degree of machinability. (See "Dowmetal" and "Elektron" Alloys.) They are widely used in aircraft construction and in applications where portability is the paramount factor. Another application of magnesium alloys is as anodes for cathodic protection of hot-water tanks and for underground pipe-lines against corrosion. (See "The Use of Magnesium Anodes for Cathodic Protection," by L. M. Oldt (*Corrosion and Material Protection*, 3, 12 (1946)); "Cathodic Production of Metals" (*Light Metals*, 9, 378 (1946)); "Magnesium as a Galvanic Anode," by H. A. Robinson (*Trans. Electrochem. Soc.*, Preprint 90-4 (1946)) and "Magnesium Anodes for the Cathodic Protection of Underground Structures," by H. A. Robinson (*Corrosion*, 2, 199 (1946)).)

*References:* *The Technology of Magnesium and Its Alloys*, by A. Beck (F. A. Hughes and Co., London); *Magnesium and its Alloys*, by J. L. Houghton and W. E. Prytherch (Chemical Publishing Co., Brooklyn, N.Y.); *Introduction to Magnesium and its Alloys*, by J. Allico (Ziff-Davis Publishing Co., New York); *Magnesium: Its Production and Use*, by E. V. Pannell (Pitman Publishing Corp., New York); *Magnesium*, by L. M. Pidgeon, J. C. Mathes, N. E. Woldman, J. V. Winkler, and W. S. Loose (American Society for Metals, Cleveland, Ohio); *Non-ferrous Melting Practice—Melting and Refining Practices for Magnesium*, by C. E. Nelson (American Institute of Mining and Metallurgical Engineers, New York); "New Developments in Magnesium Foundry Technology," by L. A. Carapella (*Aluminium and Magnesium*, 2, 10 (1946)); *Metallography of Magnesium and its Alloys*, by W. Bulian and E. Fahrenhorst (F. A. Hughes and Co., London); *Magnesium Fabrication*, by L. B. Harkins (Pitman Publishing Corp., New York); and *Designing with Magnesium* (American Magnesium Corporation, Cleveland, Ohio).

The **Oxide** ( $\text{MgO}$ ) occurs in nature in the mineral *periclase*, and is produced in the form of *calcined magnesite* when magnesium carbonate is subjected to a sustained heat. Its production from dolomite is the subject of an article by L. Cambi (*B.C.A.*, 50, B, 18 (1931)). The product when pure is white and light, and it is used as a cement owing to its double capacity of slowly absorbing carbon dioxide and moisture. When prepared by heating the carbonate to  $800^\circ\text{C}$ . and mixed with a strong solution of magnesium chloride, the mixture sets to a hard compact cement. It is also used for heat insulating, and, owing to its refractory character (m.p. about  $2,800^\circ\text{C}$ .), is of peculiar value for the manufacture of crucibles and cupels for metallurgical purposes. (See Sorel Cement, and "Xyloolith.")

**Magnesium Hydroxide** ( $\text{Mg}(\text{OH})_2$ ) is obtained as a white precipitate upon addition to a soluble magnesium salt of a solution of sodium hydroxide, and in the dry state is used in sugar-refining.

The **Peroxide**, a commercial preparation made by reaction between sodium or barium peroxide and strong solution of magnesium sulphate, is a white powder insoluble in water, used as a bleaching agent for wool and silk fabrics.

## MAGNESIUM, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country				Magnesium Metric Tons
Germany	..	..	..	14,200
United Kingdom	..	..	..	3,300
France	..	..	..	1,900
Switzerland	..	..	..	400
Italy	..	..	..	200
				<hr/>
				20,000
U.S.S.R.	..	..	..	1,000
United States	..	..		3,000
Japan	..	..	..	1,300
				<hr/>
Sum of above	..	..		25,300

World War II brought about a tremendous increase in the production of magnesium in the United States, as is shown by "apparent consumption" in 1941, 14,000 short tons; 1942, 43,000; 1943, 156,000; 1944, 142,000; 1945, 43,000

**Magnesium Oxychloride** — See Sorel Cement.

**Magnesium Sulphate** (*Epsomite*, or **Epsom Salts**) ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) (crystal system No. 4), occurs in quantity in the Stassfurt salt deposits (*kieserite*), and there are deposits in a number of places in Wyoming, Washington, Utah, and California in the U.S.A.; also in Canada and elsewhere. It mainly occurs as white, granular, fibrous, or earthy masses or in crusts, and is a common constituent of mineral waters, such as those of Epsom, in Surrey. It is readily obtained in solution from *kieserite* or by the action of sulphuric acid upon *dolomite* and separation of the insoluble calcium sulphate thus formed, and is a colourless, crystalline salt, soluble in water, used as a medicine; also in fireproofing, warp-sizing cotton goods, and as a fertilizer. Its manufacture by the "Dow" method consists in the formation of the sulphite by absorption of sulphur dioxide in magnesium hydrate and oxidation of the sulphite by blowing with air under specified conditions.

**Magnesium Alba**, of the pharmacists, is a varying mixture of magnesium carbonate and hydroxide, made by precipitating a boiling solution of magnesium sulphate with a hot solution of sodium carbonate; it is used in fireproofing and as a face-powder, etc.

**Magnesium Chloride** is a deliquescent body very soluble in water, which can be obtained in crystalline form ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ), as also in the anhydrous state ( $\text{MgCl}_2$ ) by dehydrating the crystals heated in a stream of dry hydrogen chloride gas. The crystalline form loses two molecules

of water at 100° C., and is used for dressing cotton fabrics, fireproofing wood, etc. (See Potassium Chloride.)

**Magnesium Carbonate** ( $\text{MgCO}_3$ ) — The precipitate obtained by adding an alkaline carbonate to a solution of magnesium sulphate is not a pure  $\text{MgCO}_3$ , but a basic compound of somewhat varying composition according to varying conditions of precipitation. By suspension in water and saturation with carbon dioxide, the precipitate dissolves, and only upon heating to 300° C. under pressure is the normal anhydrous carbonate deposited in rhombohedral crystals. These precipitates and the real carbonate can be used in common with natural deposits of the carbonate in admixture with asbestos for covering steam-pipes; also in fireproofing, making tooth-powders, as clarifying agents, and for preventing the formation of scale in boilers.

**Magnesium Citrate** ( $\text{Mg}_3(\text{C}_6\text{H}_5\text{O}_7)_2 \cdot 14\text{H}_2\text{O}$ ) is a soluble white salt used in medicine.

**Magnesium Nitrate** ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) is a white, crystalline salt, soluble in water, used in ceramics and pyrotechnics.

**Magnesium Fluoride** ( $\text{MgF}_2$ ) is a white, crystalline compound used in ceramics.

**Magnesium Ammonium Phosphate** ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ) is a white powder insoluble in water, used in medicine, and obtained by addition of magnesium sulphate solution to one of a phosphate solution in presence of ammonium chloride and ammonia.

**Magnesium Silicate (Talcum)** ( $3\text{MgSiO}_3 \cdot 5\text{H}_2\text{O}$ ) — A white compound, insoluble in water, prepared by interaction of a soluble silicate and a magnesium salt in solution; used in medicine.

**Magnesium Perborate** is a soluble white powder used in making driers. The **perchlorate** ( $\text{Mg}(\text{ClO}_4)_2$ ) and the **oleate** are similarly used. The perchlorate (as "Anhydrone") is used as a water absorbent in chemical analysis.

Many magnesium salts are prepared for medicinal use.

**MAGNETIC IRON ORE (Loadstone, Magnetite)** ( $\text{Fe}_3\text{O}_4$ ) — Crystal system No. 1, and sp. gr. 5.0. (See Iron and Loadstone.)

"**MAGNICO**" — A permanent magnetic alloy, claimed to be superior to the "Alnico" magnet, and composed of 12 per cent. cobalt, 6 per cent. copper, 10 per cent. aluminium, and 18 per cent. nickel thermomagnetically treated, the remainder being iron. The relative weight per unit of energy is one-fourth of that of the "Alnico" magnet, thus making it suitable for lighter magnetos. (See A. S. Zaimovski and L. M. Lvov in *Engineers' Digest* (Am.), 3, 389 (Aug. 1946).)

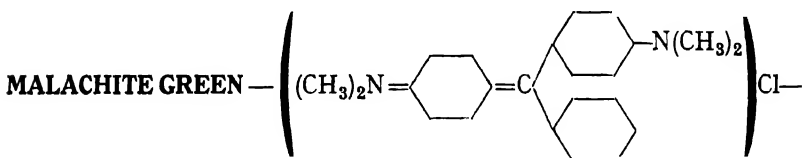
"**MAGNOLIA**" — An alloy of 80 parts lead, 15 antimony, and 5 tin; modifications are made for spindles, high-speed shafting, and dynamo bearings.

**MAHOGANY** — Wood of the *Swietenia mahogani*, N.O. Cedrelaceæ, of the W. Indies and S. America. The E. India mahogany comes from the Rohuna tree (*Soymida febrifuga*) and the African variety from the *Khaya Senegalensis*. The wood varies greatly in value in respect of each sort according to their several physical features, etc.

**MA HUANG** — See Ephedra, and Ephedrine.

**MAIZE OIL (Corn Oil)** — From the germs of Indian corn or maize plant (*Zea Mays* L.), constituting a by-product in the preparation of maize starch. It is golden-yellow in colour, sp. gr. at 25° C. 0.9105, and is composed of the glycerides of oleic acid (45.4 per cent.), linoleic acid (40.9 per cent.), palmitic acid (7.7 per cent.), of stearic acid (3.5 per cent.), arachidic acid (0.4 per cent.), lignoceric acid (0.2 per cent.), and 1.7 per cent. of unsaponifiable matter; i.v. (Hanus) 117.2, sap. v. 187.3, ref. ind. 1.4768 at 15° C. It solidifies at from -10° to -20° C. The unsaponifiable matter of the oil is stated to consist largely of a phytosterol identical with sitosterol, of m.p. 137.5° C. The seeds yield from 6 to 10 per cent. of the oil, which is soluble in ether, chloroform, and benzol; is edible, and used in soap-making, also as a rubber-filler, and for lubricating and leather-dressing. Maize is a valuable feeding-stuff and contains a protein named zein, but is deficient in the amino-acids characteristic of wheat.

**MALACHITE** (crystal system No. 5, and sp. gr. 3.75 to 4.0) — Native basic copper carbonate ( $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ) found in the Ural Mountains, in Arizona and New Mexico (U.S.A.), and elsewhere; finds use for ornamental purposes, as a mineral pigment, and a source of copper. (See Copper.)



A green crystalline dye of metallic sheen, marketed as the oxalate (Colour Index No. 657), and as the double salt of the chloride and zinc chloride. It is formed by the condensation (loss of 1 mole water) of 1 mole benzaldehyde ( $\text{C}_6\text{H}_5\text{CHO}$ ) and 2 moles dimethylaniline ( $\text{C}_6\text{H}_4\text{N}(\text{CH}_3)_2$ ) (via 2 para hydrogen atoms), followed by oxidation and salt ( $\text{ZnCl}_2$ ) formation.

Malachite green dyes cotton, mordanted by tannin, a deep green.

**MALAKON (Malacon)** — A zirconium silicate from Madagascar containing small amounts of hafnium, thorium, and other rare earths, etc.

**MALE FERN (Aspidium)** — The carefully dried rhizome of *Dryopteris Filix-mas*, collected late in the autumn and deprived of its roots and dead portions. It contains filmarone, a yellow amorphous anthelmintic principle which decomposes, in solution, into aspidinol and filicic acid. Filicic acid occurs in two forms, a crystalline variety melting at 213° to 215° C. and an amorphous form, known as filichin, which is possibly an anhydride. The ether-soluble extract of the drug is also known as filicin. An ether-extract of male fern is used in medicine for the expulsion of tape-worms.

**MALEIC ACID** ( $\text{COOH} \cdot \text{CH} : \text{CH} \cdot \text{COOH}$ , *cis*), a crystalline substance readily soluble in water which can be prepared from malic acid by distillation ; or cheaply from benzene in the vapour phase by catalytic oxidation using air over vanadium pentoxide heated.

When heated alone at  $160^{\circ}\text{C}$ ., it is converted partly to maleic anhydride (this by dehydration) and partly to fumaric acid (this by rearrangement) ; when heated in a sealed tube (water does not escape) at  $200^{\circ}\text{C}$ . fumaric acid is the principal product ; and when heated in a vacuum (water escapes) at  $100^{\circ}\text{C}$ . maleic anhydride is the product. Maleic anhydride is an important material in the production of synthetic resins.

**MALIC ACID** ( $\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$ ) — Occurs, together with citric acid, in unripe apples and many other fruits, including gooseberries, cherries, bilberries, strawberries, raspberries, tomatoes, mountain-ash berries, quinces, pineapples, etc. ; also in the roots and flowers of many other plants. The acid obtained from natural sources and by the action of yeast on sucrose solutions is lævo-rotatory, but the synthetically obtained acid is optically inactive. It is manufactured in the U.S.A. by the catalytic oxidation of benzene to maleic acid and conversion of that product into malic acid by heating with steam under pressure. A concentrated syrup left to evaporate yields the acid in the form of colourless, odourless, deliquescent needles or prisms, soluble in water, which melt at  $100^{\circ}\text{C}$ . It can be obtained from both fumaric and maleic acids in the optically inactive form by heating them with dilute alkali, and by suitable chemical treatment it can be obtained also from malonic acid. Malic acid is non-toxic and can be used as a substitute for citric and tartaric acids in beverages and for other applications. Maple sap contains calcium malate. The malates are soluble in water.

**MALLEABILITY** — See Metallography, and Metals.

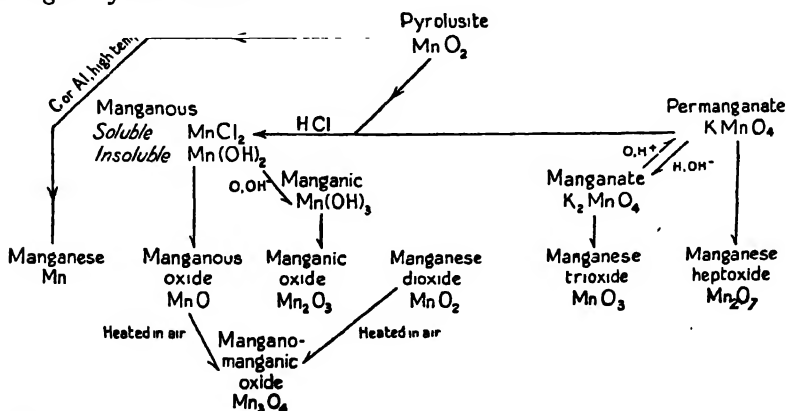
**MALLEE BARK** — The bark of *Eucalyptus occidentalis* of Queensland (which yields the Dumosa eucalyptus oil), containing from 30 to 50 per cent. tannin. (See Tannins.)

**MALONIC ACID** ( $\text{CH}_2(\text{COOH})_2$ ) crystallizes in white plates, soluble in water and alcohol, and melts at  $130^{\circ}\text{C}$ ., with decomposition. Although the acid itself is unimportant, the diethyl ester is a very important synthetic agent for the preparation of substituted acetic acids, owing to the reactivity of the two  $\alpha$  hydrogen atoms.

**MALT** — Barley or other grain the starch of which has been modified by steeping and by germinating on the malting floor so that in the mash-tun the enzyme diastase, which has increased during malting, converts the modified starch into dextrine, malto-dextrine, and maltose ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ). One ton of malt gives some 4 tons of weak extract of density  $14^{\circ}$  Balling, or 6 tons of density  $10^{\circ}$  Balling, the yield varying from 76.5 per cent. to 79.9 per cent. according to the precise conditions of the process employed. The diastatic action of malt is practically limited to the temperature range  $60^{\circ}$  to  $90^{\circ}\text{C}$ ., its activity being greatest at from  $70^{\circ}$  to  $80^{\circ}\text{C}$ ., and from three to four times greater than any of

**MANGANESE (Mn) and its Compounds** — Atomic weight, 54.93. See Elements for other data ; and also accompanying Chart. Manganese

Arrangement Based on Valency and Reduction-Oxidation Properties  
Arranged by the Editor.



## MANGANESE ORE, WORLD PRODUCTION

Annual average for the three-period period 1937-1939

Data arranged and rounded off by the Editor.

Country				Manganese Ore Metric Tons	Mn Content, %
Rumania	..	..	..	51,000	30 to 36
Italy	..	..	..	42,000	34 to 37
Hungary	..	..	..	24,000	35 to 48
				<hr/> 117,000	
U.S.S.R.	..	..	..	2,500,000	41 to 48
Cuba	..	..	..	119,000	36 to 50
U.S.A.	..	..	..	32,000	35
				<hr/> 151,000	
Brazil	..	..	..	223,000	38 to 50
Chile	..	..	..	15,000	40 to 50
				<hr/> 238,000	
British India	..	..	..	970,000	47 to 52
Malaya	..	..	..	32,000	30
Philippines	..	..	..	30,000	35 to 48
Netherlands Indies	..	..	..	10,000	50 to 55
				<hr/> 1,042,000	
Union of South Africa	..	..	..	534,000	30 to 51
Gold Coast	..	..	..	444,000	50
Egypt	..	..	..	153,000	30
French Morocco	..	..	..	79,000	40 to 50
				<hr/> 1,210,000	
Sum of above	..	..	..	5,258,000	
WORLD PRODUCTION	..	..	..	5,500,000	

Manganese ore is also produced in Belgian Congo, Bulgaria, China, Greece, Indochina, Iran, Northern Rhodesia, Portuguese India, Puerto Rico, Queensland, Sweden, Turkey, Yugoslavia.

is found in nature chiefly in the form of *pyrolusite*, a black oxide, of sp. gr. 4.8 to 5.0, containing from 70 to 80 per cent. of dioxide ( $MnO_2$ ). Among other ores may be enumerated *braunite*, a manganese ore of the composition  $Mn_2O_3$ , crystal system No. 2, and sp. gr. about 4.7, occurring in Sweden, the U.S.A., and India; the red mineral *hausmannite* ( $Mn_3O_4$ ); *manganite*, a hydrated oxide ( $Mn_2O_3 \cdot H_2O$ ), of crystal system No. 4, and sp. gr. 4.2; *manganese spar* (*rhodonite*), a carbonate ( $MnCO_3$ ); and *manganese blende*, a native sulphide ( $MnS$ ).

Manganiferous iron ore and other deposits occur abundantly in Spain, French Morocco, the U.S.A., Georgia, Canada, India, Brazil, Russia, Cuba, at Postmasburg near Kimberley (South Africa), and Insuta (West Africa). The South African ore is low in phosphorus and silica content, and is stated on average to contain 53.5 per cent. manganese, 5.84 per cent. silica, 4.5 per cent. iron, and 0.059 per cent. phosphorus.

Metallic manganese can be obtained by reduction of the oxide with carbon in an electric furnace, but is commercially prepared by using powdered aluminium for reduction of the oxide in a refractory furnace, the mixture being ignited by means of a fuse. When required in a purer state, fused anhydrous manganese chloride is reduced by heating with metallic magnesium. This procedure is also employed in the commercial preparation of the magnesium-manganese alloy. (See references under Magnesium.) Still another commercial process for the production of manganese metal is electrolytic reduction which has received wide attention in the United States. See paper on "The Present Status of Electrolytic Manganese and Its Alloys," by R. S. Dean (*Trans. Amer. Soc. Mech. Engrs.*, **156**, 301 (1944)).

Pure manganese is greyish-white, is attacked by dilute acids, and has at least three allotropic modifications. It is normally brittle, but in the gamma form the metal is relatively ductile. Manganese is very important in steel-making as a deoxidizer, desulphurizer, and recarbonizer, and as an alloying element. High-manganese steels are tough, non-magnetic and resistant to abrasion. They find a wide range of uses in armaments, mining, milling, digging, etc. It alloys also with many non-ferrous metals such as aluminium, copper, magnesium, and nickel. Manganese with around 18 per cent. copper manifests a pronounced damping capacity or deadness when struck and lacks the metallic ring. (See the paper on this subject by R. S. Dean and his co-workers in *Trans. Amer. Soc. Metals*, **29**, 402 (1941)). Manganese is added to aluminium, bronze, and magnesium to give toughness and resistance to corrosion. Manganese alloys are generally employed in manufacturing of many materials with important mechanical and electrical properties. (See Iron (Ferro Alloys).)

**Oxides** — Of these, the most important members are the dioxide ( $\text{MnO}_2$ ) (black oxide of manganese), and the monoxide ( $\text{MnO}$ ), followed, in order of diminishing importance, by manganomanganic oxide ( $\text{Mn}_3\text{O}_4$ ), and the sesquioxide ( $\text{Mn}_2\text{O}_3$ ), and, finally, by the heptoxide ( $\text{Mn}_2\text{O}_7$ ) (an explosive brown liquid), and the trioxide ( $\text{MnO}_3$ ).

Manganese dioxide can be prepared by adding a solution of bleaching powder to a manganous solution or by roasting the monoxide in oxygen. It can also be prepared from any lower oxide by direct oxidation with oxygen, using sodium hydroxide as catalyst at from  $400^\circ$  to  $500^\circ$  C. The air-dried product is  $\text{MnO}_2 \cdot \text{H}_2\text{O}$  (Kato and Matsushashi, *B.C.A.*, **A**, 1930, 308). When dried and heated to redness it decomposes, becoming reduced to a lower oxide and giving off oxygen gas, thus:  $3\text{MnO}_2 = \text{Mn}_3\text{O}_4 + \text{O}_2$ . Manganese dioxide acts the part of a weak acid in  $\text{CaO} \cdot \text{MnO}_2$ ,  $\text{CaO} \cdot 2\text{MnO}_2$ , and  $\text{CaO} \cdot 5\text{MnO}_2$ , compounds

that are supposed to be constituents of the so-called Weldon mud. (See Chlorine.) It is employed in the manufacture of chlorine and as an oxidizing agent, also in the paint and varnish trades as a drier, and is the principal mineral source of manganese element.

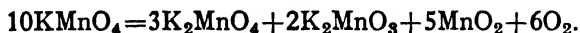
**Manganese Hydroxide** ( $\text{Mn}(\text{OH})_2$ ), obtained by adding sodium hydroxide solution to a manganous solution, is a nearly white gelatinous mass which becomes rapidly brown in colour by absorption of oxygen from the air, thus passing into one of the higher oxides. It finds use as a pigment and in the ceramic industries.

**Manganate and Permanganate of Potassium** — Potassium permanganate ( $\text{KMnO}_4$ ) is used in nickel refining, and both it and the manganate ( $\text{K}_2\text{MnO}_4$ ) as sanitary reagents, being valued on account of their oxidizing properties. There are corresponding sodium compounds, and all are used in oxidizing, tanning, and bleaching processes.

By fusing in air the black oxide of manganese together with potassium hydroxide or carbonate, the green manganate is obtained by dissolving the product in water:  $4\text{KOH} + 2\text{MnO}_2 + \text{O}_2 = 2\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O}$ ; whilst the crystalline red permanganate is chiefly made by the electrolysis of the manganate solution at a temperature of about  $60^\circ \text{C}$ ., using iron electrodes.

Another method of manufacturing potassium permanganate consists in first of all making sodium permanganate by fluxing manganese ore with caustic soda (with or without the addition of sodium nitrate as an oxidant), dissolving the product after grinding in water, and treating the solution with chlorine and sulphuric acid, or alternatively with carbon dioxide, to transform the manganate into permanganate of sodium, and subsequently mixing the filtered concentrated permanganate liquor with the theoretical amount of potassium chloride, and again concentrating the mixture by heat, when the potassium permanganate crystallizes out upon cooling.

When heated to  $200^\circ \text{C}$ . the permanganate begins to decompose, and the decomposition is completed at  $240^\circ \text{C}$ ., as represented by the equation:



**Manganese Chloride** ( $\text{MnCl}_2$ ) is a soluble salt which can be obtained in crystalline form as  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ , and is used as a drier in oil-boiling; also in dyeing and calico-printing.

**Manganese Sulphate** ( $\text{MnSO}_4$ ) can be obtained in crystalline form combined with water ( $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$ ); is used in ceramics and textile dyeing, and marketed of 95 per cent. strength.

**Manganous Sulphide** ( $\text{MnS}$ ) is a flesh-coloured, insoluble compound, obtained by adding an alkaline sulphide solution to one of a manganous salt.

**Manganous Carbonate** ( $\text{MnCO}_3$ ) in precipitated form is a slightly rose-coloured, insoluble body used in the pottery trade. In native form it occurs as an ore in Wales, but as an outcrop it is transformed into hydrated black oxide.

**Manganese Borate** is a white powder, prepared by precipitating solutions of manganese salts with one of borax, and has, when dry, the composition  $\text{MnH}_4(\text{BO}_3)_2 \cdot \text{H}_2\text{O}$ , losing its water of crystallization upon heating to  $100^\circ \text{C}$ ., and at higher temperatures becoming  $\text{Mn}(\text{BO}_3)_2$ . It is marketed as of 85 per cent., and used as a drier for varnishes and in the oxidation of linseed oil, being superior to lead driers but inferior to manganese dioxide, having, however, the advantage of not darkening the oil so much.

**Manganese Resinate** ( $\text{Mn}(\text{C}_{20}\text{H}_{29}\text{O}_2)_2$ ) — A dark, nearly black substance, prepared by boiling manganese hydroxide with rosin oil and water. It is soluble in hot linseed oil, and is used in common with manganese borate and manganese oleate as a varnish and oil drier. A manganese drier is also prepared by heating together common resin and manganese dioxide in certain proportions.

**Manganese Oleate** ( $\text{Mn}(\text{C}_{18}\text{H}_{33}\text{O}_2)_2$ ), also used as a drier, is prepared by boiling manganese chloride with sodium oleate and water, and is a dark brown substance soluble in oleic acid.

**Manganese Acetate** ( $\text{Mn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 4\text{H}_2\text{O}$ ) — A pale red crystalline salt, soluble in water; used as a drier, also in textile dyeing and manufacturing bistre (a brown pigment made from soot).

**Manganese Silicate** ( $\text{MnSiO}_3$ ) is a red, crystalline, insoluble substance used for colouring glass, and in ceramics.

The salts of manganese are flesh or pink coloured.

Manganese salts are said to serve as plant stimulants, particularly in respect of marl soils.

**MANGANESE STEEL** — See Iron (Steel), and Manganese.

**MANGANITE** — See Manganese.

**MANGOSTIN** — See Gums and Resins

**MANGROVE** — A tannin material (cutch) containing from 35 to 40 per cent. tannin, derived from the mangrove (*Rhizophora mangle*), growing in Mozambique, Parapet, Pomba Bay, parts of East and West Africa, S. America, China, and Borneo.

**MANILA GUM** — See Gums.

**MANILA HEMP** — Fibre used for making certain qualities of cigarette and other papers, rope, hawsers, string, etc. (See Hemp, and Sisal.)

**MANIOC (Manihot)** — See Cassava, and Tapioca.

**MANNA** — The dried juice or sweet sap from incisions made in the stems of certain species of the manna ash (*Fraxinus ornus* and *F. rotundifolia*), which grow in Calabria, Sicily, and in the East. It contains from 30 to 60 per cent. of mannitol ( $\text{C}_6\text{H}_{14}\text{O}_6$ ), which can be extracted by hot alcohol. (See Mannitol.)

**MANNANS** — See Mannose.

**MANNITOL (Mannite)** ( $\text{CH}_2\text{OH}(\text{CHOH})_4\text{CH}_2\text{OH}$ ) — The chief constituent of manna, and found present in *Myoporum laetum* (Forst), a tree indigenous in New Zealand: 0.2 per cent. in the berries and 0.25 per cent. in the wood. It is a white, crystalline body, soluble in water

and to some extent in alcohol, and can be produced by the action of sodium amalgam on the mixture of dextrose and lævulose that results from the action of dilute sulphuric acid upon cane sugar when boiled together. It is not very sweet, melts at about  $160^{\circ}\text{C}.$ , and by the action of dilute nitric acid is converted into mannitic acid ( $\text{C}_6\text{H}_6\text{O}(\text{OH})_6$ ). Chemically, it is regarded as a polyhydric alcohol derived from mannose, the last-named substance being stereoisomeric with one of the glucoses comprehended in the monosaccharoses. (See Carbohydrates.) It can be made to replace glycerol in fat (see Olive Oil); can be distilled without appreciable decomposition; does not ferment except under unusual conditions, and has been synthesized. *d*-Mannitol is made commercially from dextrose, and is used in making resins, plasticizers, laxatives, pharmaceutical preparations, and in organic syntheses. (See Manna.)

**MANNOSE** — A monosaccharide occurring naturally in the form of condensation products known as mannans, and from which it can be obtained by acid or enzymic hydrolysis. Vegetable ivory (the kernel of the nut of *Phytelephas macrocarpa*) constitutes a convenient source.

Chemically, mannose is very similar to glucose, differing from it only in the configuration of the carbon atom adjacent to the terminal aldehydic group. (See *An Introduction to the Chemistry of Carbohydrates*, by Honeyman (Clarendon Press, Oxford); and Vegetable Ivory.)

**MANOMETER** — Instrument for measuring the tension of gases, steam, etc.; a pressure gauge.

**MANUKA OIL** — The essential oil from the leaves and terminal branchlets of *Leptospermum scoparium*; yield 0.37 per cent. by weight; soluble in 10 vols. of 90 per cent. alcohol. It contains 12 per cent.  $\alpha$ -pinene, 60 per cent. eudesmene and another semiterpene, 6 per cent. citronellol, geraniol, etc., 1 per cent. citronellal and citral, 1 per cent. cineol, and 12 per cent. other constituents; sp. gr. 0.918.

**MAPHARSIDE (Mapharsen)** — See Arsphenoxide.

**MAPLE SUGAR** — See Sugar.

**MARBLE** — Crystalline limestone. (See Calcium.)

**MARC** — The refuse material left after extraction or pressure of seeds, fruits, and herbs.

“**MARFANIL**” ( $\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2\text{S}\cdot\text{HCl}$ ) — A German drug, being the hydrochloride of 4-aminomethylbenzenesulphonamide ( $\text{H}_2\text{N}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2$ ); freely soluble in water. It is not inactivated by the presence of pus or *p*-aminobenzoic acid as are the other members of the sulphonamide series and has been recommended for local application to wounds. (See Sulphanilamide.)

**MARGARIC ACID** ( $\text{C}_{16}\text{H}_{33}\cdot\text{COOH}$ ) — One of the higher fatty acids, melting at  $60^{\circ}\text{C}.$ , and boiling at  $227^{\circ}\text{C}.$  at 100 mm. pressure.

**MARGARINE** — A butter substitute, manufactured on a large scale, consisting of fatty acids or oils from various sources, compounded with skim-milk sterilized by heating from  $60^{\circ}$  to  $82^{\circ}\text{C}.$ , and inoculated with

the butyric ferment (lactic acid bacilli), carefully grown in milk, in order to give the blended mixture a butter-like odour.

Cotton-seed, palm, coconut, and arachis oils are largely used, and in some cases animal fats, such as "premier jus" and lard, are admixed with the vegetable oils, so proportioned as to give a m.p. of about 22° to 27° C. Stearine, being more solid at the ordinary atmospheric temperature, is also used when necessary to counteract the more liquid oils and to adjust the desired consistency. The fats produced by the hydrogenation process (see Hydrogen (Hydrogenation)), from whale, cotton-seed, and other oils, are now also extensively used to replace the animal fats previously employed.

The process of making is somewhat as follows: the milk, after cooling to 10° C., is churned with the melted mixture of fats and oils at a temperature of 25° to 35° C. until thoroughly emulsified, then rapidly cooled, and after maturing (to allow the butyric ferment to do its work), kneaded to expel the excess of water over 16 per cent., which is the legal limit. It is essential that the oils should be run slowly into the milk in the churn, to produce a fine-grained permanent emulsion of the oil-in-water type, as if the reverse method be used, an emulsion of the water-in-oil type results, and is not so satisfactory. Addition of vitamins makes the product comparable in food value with butter, and cheaper than the latter. (See Emulsions.)

**MARIGOLD** (*Calendula*) — The dried florets of *Calendula officinalis* (Fam. Compositæ); a native of France and some southern parts of Europe. It contains calendulin, a yellow colouring matter, and is used in colouring butter and cheese.

**MARINE GLUE** is a cementing composition consisting of rubber and shellac dissolved to a paste in naphtha.

**MARJORAM OIL** — The essential oil distilled from the aromatic herb *Origanum marjorana* and other species (Fam. Labiatae), cultivated in Spain, Morocco, and Tunisia. It contains sabinene, terpineol, borneol, and terpenes; is soluble in alcohol and ether, and used for scenting soap, and in perfumery. Its sp. gr. is 0.894 to 0.912 at 15° C., opt. rot. +5° to +18° at 20° C., and ref. ind. 1.4725 to 1.4765 at 20° C. The fresh herb is stated to yield 0.35 per cent. oil.

**MARKING INKS** — See Inks.

**MARL** — Earth consisting of clay, chalk, and sand.

**MARMATITE** — A ferruginous variety of blende (in which zinc is partly replaced by iron and manganese) occurring in the Broken Hill concentrates.

**MAROTI OIL** — From the seeds of *Hydnocarpus Wightiana* (Blume); sp. gr. at 25° C. 0.956, sap. v. 199 to 201, and i.v. (Winkler) about 93 to 96.

**MARSH GAS** — A mixture of methane (CH<sub>4</sub>) (a constituent of coal gas) with carbon dioxide and nitrogen, formed in nature by the decomposition of organic bodies under water. (See Hydrocarbons (Methane).)

**MARSH'S TEST** — See Arsenic (Hydride).

**MARTEMPERING** — Heat treatment of steel in which martensite is produced with minimal residual strains, thereby eliminating quench-cracks and distortion. In this treatment the steel is rapidly quenched in a special bath, held at a constant temperature which is just above the austenite-martensite transformation temperature, and as soon as equalization in temperature has been realized in the mass, it is removed and allowed to air cool.

**MARTENSITE** — A transformational product of austenite found in quenched hardened carbon steels. For further reference see "The Martensite Transformation" by A. R. Troiano and A. B. Greninger in *Metal Progress*, **50**, 303 (1946); and "Computing Martensite Transformation Temperatures from Analyses," by L. A. Carapella in *Metal Progress*, **46**, 108 (1944); and Iron.

**MASS ACTION** — See Elements, Esters and Esterification, and Chemical Interactions.

**MASS-ENERGY EQUIVALENCY** — See Energy, Nuclear Chemistry, and Matter.

**MASS NUMBER** — The total number of protons and neutrons in the nucleus of an atom, approximately the atomic weight. It is to be distinguished from atomic number, which gives the number of protons in the nucleus and at the same time the number of electrons outside the nucleus.

**MASS-SPECTROGRAPH** — The mass-spectrograph is an instrument by means of which the charged atoms in a beam of positive rays are sorted out according to their masses by the use of magnetic and electric fields, so that atoms of different masses strike a photographic plate at different points. In this way a mixture of atoms of differing weights gives a series of focused lines (mass-spectrum), enabling their relative weights to be calculated from the positions of the lines. It is in this way that the so-called isotopes are identified, chlorine, for example, being thus viewed as a mixture of atoms of weights 35 and 37. In such investigations in which very minute quantities of materials are dealt with, the question of their absolute purity is of great importance, and they may possibly be contaminated with hydrogen, mercury from the vacuum pump, or other impurities associated with or derived from the apparatus or its atmospheric environment.

Precise atomic weights of the lighter elements—to the fifth decimal place—are determined with the mass-spectrograph, and this instrument is used for the analysis of organic compounds, especially hydrocarbons. (See *Mass Spectra and Isotypes*, by F. W. Aston (Longmans, Green and Co., London and New York); Atoms, Elements, and Spectroscopy.

**MASSICOT** — See Lead.

**MASTER ALLOY** — A metallic mixture, rich in one or more desired components, employed as a convenient means of preparing other alloys with different metals.

**MASTIC** — See Asphalt, and Gums and Resins.

**MASURIUM** — See Technetium.

**MATCHES** — Splints of wood, sometimes immersed in melted paraffin wax and then tipped by dipping into some igniting compound, of which there are many varieties. Some "safety" types of matches are tipped with a mixture of potassium nitrate or chlorate, potassium dichromate, red-lead, and antimony sulphide, held together with a glue binder, so that when rubbed over a surface of material containing the non-poisonous amorphous form of red phosphorus in admixture with sulphide of antimony with which the striking sides of the match-boxes are covered, they take fire by friction. Paper board is commonly used instead of wood for the body of matches.

In recent years the use of phosphorus has been supplanted by that of sesquisulphide of phosphorus. In the United States this dates from about 1912 when Federal legislation made it advantageous to change the process as stated.

According to an invention of M. M. Dessau, matches are water-proofed by incorporating rubber latex with the fulminating material, and then vulcanizing by the Peachey process. (See Rubber.) They are treated for prevention of after-glow by impregnating with various salts. (See Fire Proofing.)

"Vestas," or wax matches, only differ from the wooden ones in respect of the nature of the stalks, and "Vesuvians" in respect of the bulbous head, which is formed of some such mixture as charcoal, nitre, sand, and some binding material, tipped with the igniting mixture.

Flame-producing devices are used as substitutes in part for matches.

**MATÉ (Paraguay Tea)** — Leaves of *Ilex paraguayensis*, containing about 2 per cent. caffeine, steeped and used as a beverage by South American peoples.

**MATERIAL BALANCE** — A quantitative statement of all material entering and leaving a piece of apparatus, or any part of it, in a given time. In accordance with the Law of Conservation, the total amount of matter entering must equal that leaving plus any accumulation in, or minus any loss from the region considered. Material balances are constantly used in chemical engineering design. They may be drawn up with respect to (a) a complete process plant, (b) a single piece of equipment, or (c) some part of a piece of equipment—for example, one plate of a fractionating column. Types (a) and (b) give a concise statement of input and output and furnish data for Flow Sheets (*q.v.*). Type (c) is often of the greatest value in the theoretical analysis of chemical processes and unit operations.

**MATERIALS OF CONSTRUCTION** — Generally speaking, corrosion resistance is the most sought-after property in materials for chemical service. Corrosion rates depend largely on conditions of service, and the following notes are only a rough guide. When corrosive materials have to be handled, it is always advisable to make practical tests before finally selecting materials of construction. One of the functions of a pilot plant is to furnish such tests.

**Iron.** It was formerly thought that cast iron resisted corrosion better than wrought iron or steel. Later experiments do not support this view. Castings are normally thicker than fabricated steel vessels, and when new they may have a slight protective skin, but otherwise there seems to be little difference in the corrosion resistance of the three materials.

Iron resists anhydrous acids, alkalis, and dry halogen gases. It is used for sulphuric acid above 80 per cent. strength, and withstands oleum in all concentrations except in the immediate neighbourhood of 101 per cent., where the rate of attack increases sharply (M. G. Fontana, *Ind. Eng. Chem.*, 40, 103A (1948)). It is attacked by dilute acids, organic acids, and solutions of copper salts.

**Stainless Steels** (Fe-Cr-Ni) depend for their corrosion resistance upon proper heat treatment. They differ from ordinary steel chiefly in resisting atmospheric oxidation, some organic acids, and dilute sulphuric acid below 10 per cent. strength, but they are less resistant to alkalis than ordinary steel. Stainless steels retain their strength at high temperatures much better than ordinary steel.

**Silicon Iron** (14–16 per cent. Si) withstands nitric and sulphuric acids at all concentrations and temperatures. It is attacked by hydrochloric acid, and is less resistant to caustic alkalis than cast iron or steel. Silicon iron is hard and brittle, and can only be worked by casting and grinding.

**Aluminium** resists cold nitric acid in all concentrations, most organic acids with the exception of formic, and ammonia. It is attacked by hydrochloric acid, sulphuric acid, and alkalis.

**Copper** resists non-oxidizing acids and caustic alkalis. It is strongly attacked by oxidizing acids, ammonia, and ammonium salts.

**Bronzes** are stronger than copper and less liable to oxidize. A leaded bronze containing 85 Cu, 5 Sn, 5 Zn, 5 Pb ("Ounce Metal") has been used with cold sulphuric acid of 60–90 per cent. strength.

**Brasses** are also stronger than copper, but are inferior in corrosion resistance, being liable to dezincification by both acids and alkalis. 85/15 red brass has been used with cold sulphuric acid of 60–90 per cent. strength, but it has a limited life and is less satisfactory than leaded bronze.

**Aluminium Bronze** (90 Cu, 10 Al) has good mechanical and corrosion-resisting properties. It is used for condenser tubes, and will resist cold dilute sulphuric acid up to 10 per cent. strength.

**Lead** is fairly resistant to most acids, and is the usual material for sulphuric acid from 10 to 60 per cent. (hot) or 80 per cent. (cold). Above 90 per cent. it is rapidly attacked. It resists dilute hydrochloric acid moderately well, but is attacked by nitric acid and alkalis. The mechanical strength of lead is improved by the addition of 3 per cent. antimony.

**Nickel** withstands atmospheric oxidation, concentrated caustic alkalis, and dry chlorine, and is fairly resistant to dilute acids. It is only slightly attacked by ammonia.

**Monel Metal** (67 Ni, 30 Cu, balance Fe, Mn, C, Si) has similar pro-

perties to nickel. It resists sulphuric acid better and can withstand strengths up to 75 per cent. cold, but is less resistant to ammonia.

*Hastelloy* (Ni-Mo-Fe) withstands hydrochloric acid at all concentrations and temperatures.

*Glass* and *Vitreous Enamels* resist all acids except hydrofluoric, but are attacked by concentrated alkalis.

*Stoneware* has the corrosion resistance of glass and is less fragile, but its thickness is a drawback where heat transfer is involved.

*Wood* is fairly resistant to cold dilute acids and alkalis.

*Concrete* is generally porous unless waterproofed, *e.g.*, with aluminium soaps. It resists ammonia and organic solvents, but is attacked by acids and strong alkalis. Concrete vessels are often lined with asphalt or rubber.

*Asphalt* resists cold dilute acids, but is attacked by hot alkalis and organic solvents.

*Rubber* withstands cold dilute acids and alkalis, but is softened by organic solvents. Neoprene has a greater resistance to hydrocarbons than natural rubber. Soft rubber is very resistant to abrasion, and has been used to line chutes carrying ores.

*Phenolic Resinoids* ("Bakelite", "Haveg", etc.) resist dilute sulphuric and cold concentrated hydrochloric acids, but not nitric acid or alkalis. They are insoluble in most organic solvents.

*Structural Carbon* withstands nearly all chemicals except strong oxidizing agents. It is brittle and of low tensile strength, but has a higher thermal conductivity than ceramic materials. Tubular heat exchangers have been made of it.

*References*: Perry, *Chemical Engineers' Handbook* (McGraw-Hill Book Co., New York); L. Clarke, *Manual for Process Engineering Calculations* (McGraw-Hill Book Co., New York); P. C. Carman, *Chemical Constitution and Properties of Engineering Materials* (Arnold and Co., London); James A. Lee, *Materials of Construction* (McGraw-Hill Book Co., New York); *Ind. Eng. Chem.*, **39**, 1193 (1947) and annually since 1947; *Chem. Met. Eng.*, Nov. 1950, Nov. 1948, Nov. 1946, Sept. 1944, Sept. 1942, Sept. 1940, Sept. 1938, Oct. 1936, Sept. 1934, Sept. 1932, Sept. 1929, Oct. 1926, July 1924, April 1923.

**MATLOCKITE** — A lead ore of crystal system No. 4, and sp. gr. 7.2.

**MATTE (Mat)** — See Copper.

**MATTER** — Matter is defined as anything that occupies space and possesses mass or weight. This definition is not very satisfying, because it uses the terms space, mass, and weight which themselves are not easy to define or understand. Probably the best way to understand matter is to describe its forms, properties, and transformations. Space like matter defies definition, on the other hand, mass and weight can be elucidated. We often use the terms mass and weight interchangeably, which is all right as long as we remain in a given locality, because there is a definite relation between the two in any given location. However, there is a fundamental difference between the

two terms as can be seen in the following example. Mass and weight are measured by means of instruments called balances or scales. First consider an analytical type balance which is an instrument for measuring mass or weight. It consists of a beam resting on a fulcrum having two arms; on one is placed the unknown object and on the other the known weights used to obtain a balanced condition. Next, consider a spring balance containing a spring mechanism that has been calibrated by a known weight at a given location. An unknown object will weigh the same on both the analytical and spring balance if weighed at the place where the spring balance was calibrated. Now transport both balances, the standard weights, and the unknown object to a new location, say the moon, and again measure the unknown on the two balances. This time the analytical balance will show the unknown to be balanced by exactly the same weights as before, but the spring balance will measure the weight of the object at about one-sixth of what it previously did on earth (the moon's gravitational force is about one-sixth of the earth's gravitational force). It is evident that in transferring positions we have not lost any of the matter in either the balances, the unknown, or the standard weights—this we call *the mass*. There has been a change, however, in the attractive force of the earth and moon for the object; that is, *the weight* has changed. Weight is the result of a force acting on a mass. If the force is constant then mass and weight can be used interchangeably, but if the force changes then mass and weight cannot be used interchangeably.

The mass property of matter can be further clarified by defining mass as the property that gives matter inertia. By inertia we mean that if a body is at rest it will resist any force to set it in motion, or if in motion the body will resist any force that tries to stop its motion. If this force is measured we have a measure of the inertia of the body. If we measure the force necessary to overcome the inertia, we are measuring the mass of the body. If, however, we employ the force of gravity, which is variable, for this purpose, the result is called the weight of the body.

Although the outward form or condition of matter may be radically changed, its mass remains constant (see Energy, and Chemical Interactions) in all "ordinary changes." In 1905 Einstein related mass to energy by the equation  $E=mc^2$  (where  $E$  is the energy,  $m$  the mass, and  $c$  the velocity of light). The amount of energy equivalent to mass in "unusual changes" calculated by the Einstein relationship is large; for example, one gram of matter is equivalent to  $9 \times 10^{20}$  ergs, or  $9 \times 10^{13}$  joules, or 21.5 million million calories, or 25,000,000 kilowatt hours of energy.

The properties of matter are all those marks or characteristics used to identify a substance such as colour, hardness, lustre, transparency, solubility, melting point, boiling point, density, refractive index, viscosity, electrical conductivity, heat conductivity, crystalline form, and chemical activity. Most of these properties are modified by the physical conditions under which they are observed. For example, red mercury oxide turns black upon being heated, and when cooled again

becomes red ; most liquids become less dense as the temperature increases.

Matter is made up of particles (see Atoms, and Molecules), as is evidenced by the solution of solids, the observation of Brownian motion, the scintillations of a spinthariscopescope, and the workings of a Geiger counter. In any system of matter made up of particles (atoms, molecules) there is an equilibrium between the "forces of attraction" and the "tendency to escape." The forces of attraction that are implied here are entirely physical in nature and are called van der Waals forces. These forces are very large, about  $10^{10}$  times the force of gravity, but are of short range, that is, the forces fall off rapidly with distance. The tendency for particles to escape is directly tied up with the kinetic and vibrational energy of the particles (called thermal energy). The kinetic energy is large ; for example, a hydrogen molecule at  $0^{\circ}\text{C}$ . moves with a velocity of about  $1.84 \times 10^5$  centimetres per second. The kinetic and vibrational motions of the particles of matter are directly proportional to the temperature of the matter, that is, to the intensity of heat energy. In the case of gaseous systems all gases at the same temperature have identical kinetic energies (not velocities).

The state of a given piece of matter is determined by the equilibrium that exists between the "attractive forces" and the "escaping tendencies"—the kinetic energy due to the temperature or the "thermal forces." If the "attractive forces" are much greater than these "thermal forces" then matter will assume a rigid, well-defined, dense shape that resists flow or shearing forces and it will have mechanical strength. This is called the *solid state*. When heat is applied to a solid the "thermal forces" begin to overcome the "attractive forces" and there comes a time when the solid loses its rigidity and begins to flow. We say the solid melts and enters the *liquid state*. The temperature at which this transition occurs is called the melting point of the substance. As more heat is applied the liquid becomes less dense and its vapour pressure (see same) begins to rise rapidly, until finally, if it is a system in an open vessel, the liquid begins to boil and enters the vapour or *gaseous state*, where the "attractive forces" have little opportunity to function because the molecules are so far apart. In this condition matter tends to fill all available space and is much less dense than in the liquid or solid state. The above process can be reversed by removing heat and thus increasing the attraction force/thermal force ratio. The gas would liquefy at the boiling point of the substance and the liquid would solidify at its freezing point (melting point).

Thus we see that the essential difference between the three states of matter (gas, liquid, and solid) is primarily one of temperature, that is the kinetic energy of the fundamental chemical particles (atoms and molecules) of matter. Theoretically, all matter can exist in either of the three states of matter, depending upon its relative temperature and upon obtaining the right external environment. Under ordinary conditions (pressure, atmospheric composition, etc.) many substances

decompose before the temperature is reached at which they would change their state; for example, wood heated in the absence of air will become charcoal and liberate a large number of volatile products.

A more detailed examination of the states of matter and the transitions of one state of matter to another is now in order.

I. A **gas** or **vapour** is regarded as matter in such a state that it diffuses uniformly throughout the container in which it is confined. If a substance exists completely in the gaseous state at ordinary temperatures and pressures we call it a gas; if it is ordinarily a liquid or solid, but readily vaporizes we refer to the evaporated (gaseous) portion as a vapour. Thus we speak of oxygen gas, water vapour, and camphor vapour at room temperature. The particles of a gas are generally the molecules of the substance.

The physical conduct of all gases is very nearly the same and bears no relation to the chemical composition of the gases. Consequently, the following characteristics apply generally to all substances in the gaseous state: (a) *Expansibility and compressibility*. These are properties demonstrated when the temperature or pressure is changed in a gaseous system. The relationships governing these properties are given by Boyle's and Charles' laws (see Gas Laws). These properties are due to the fact that the actual volume of the molecules in the gaseous state occupies only a small fraction of the total space in which the molecules are moving, therefore compression merely moves the molecules closer together and expansion allows them to move farther apart. (b) *Diffusibility*. The tendency of the molecules of gases to distribute themselves uniformly in any given space regardless of the presence or absence of other gases. All gases are completely miscible one in the other. This property is due to the kinetic energy of the gas molecules and their elastic bombardment upon collision one with the other or with the sides of the container. The law of diffusion was enunciated by Graham (see Gas Laws). (c) *Liquefiability*. In order to liquefy a gas two conditions must be fulfilled. First, the attraction force/thermal force ratio must reach a critical value for each gas. That is to say, the temperature must be lower than some critical value which will allow the molecular attractive forces to become effective. Second, there must be a pressure applied to force the molecules close enough together to allow the molecular attractive forces to operate. In the light of the above two conditions there must needs be a set of critical values that each substance will have in order to change from a gas to a liquid. These values are: the critical temperature—that temperature above which a gas cannot be liquefied by pressure alone; the critical pressure—the pressure necessary to liquefy a gas at the critical temperature; the critical volume—the volume of the gas at its critical temperature and pressure; the critical density—the reciprocal of the critical volume. The accompanying table displays the critical values of some typical substances.

An apparatus used to liquefy a gas will consist of the following parts: a gas intake and wash where the moisture and soluble impurities can be removed; a compression pump followed by a cooler to remove the

## CRITICAL CONSTANTS OF VARIOUS SUBSTANCES

Gas	Critical Temperature (° C.)	Critical Pressure (Atmospheres)	Critical Density (Gm. per c.c.)
Acetylene .. ..	36	62	0.231
Ammonia .. ..	132.4	111.5	0.235
Argon .. ..	-122	48	0.531
n-Butane .. ..	15.3	36	—
Carbon dioxide .. ..	31.1	73.0	0.460
Carbon monoxide .. ..	-139	35	0.311
Chlorine .. ..	144.0	76.1	0.573
Ethane .. ..	32.1	48.8	0.21
Ethanol .. ..	243.1	63.1	0.276
Ether .. ..	193.8	35.5	0.263
Ethylene .. ..	10	51	0.22
Helium .. ..	-267.9	2.26	0.069
Hydrogen .. ..	-239.9	12.8	0.031
Hydrogen chloride .. ..	51.4	81.6	0.42
Hydrogen sulphide .. ..	100.4	88.9	—
Mercury .. ..	>1,550	>200	—
Methane .. ..	-82.5	45.8	0.162
Methanol .. ..	240.0	78.7	0.272
Methyl chloride .. ..	143.1	65.8	0.37
Neon .. ..	-228.7	25.9	0.484
Nitric oxide .. ..	-94	65	0.52
Nitrogen .. ..	-147.1	33.5	0.311
Nitrous oxide .. ..	36.5	71.7	0.45
Oxygen .. ..	-118.8	49.7	0.430
Propane .. ..	95.6	43	—
Propylene .. ..	92.3	45.0	—
Sulphur dioxide .. ..	157.2	77.7	0.52
Water .. ..	374.0	217.7	0.4

The larger the attractive force/thermal force ratio, which is the same as saying the lower the temperature, the smaller the pressure needed to liquefy a gas.

heat of compression (this may be a multiple-stage system); a well-insulated chamber where the highly compressed gases are allowed to expand to a much lower pressure and in so doing become much colder; the cold gases are allowed to cool the compressed gases further until a temperature low enough to cause the gases to liquefy is reached; the non-liquefied gases are recycled through the system.

When a gas is cooled down it loses an amount of heat equal to its specific heat times its mass for every degree drop in temperature. However, when the gas has arrived at its condensation temperature a

much larger quantity of heat must be lost before the gas changes state, without a temperature change. This amount of heat energy, called the heat of condensation, is due to the large change in kinetic energy suffered as a substance goes from the gaseous to the liquid state. The heat of condensation is a characteristic of each substance. For water it is about 540 calories per gram at 100° C., for acetone about 125 calories per gram at 56° C. (see Heat (Thermochemical Aspects), and Vapour Pressure).

**II. Liquids** retain their own volume regardless of the size of the container. Because of their mobility (flow) liquids take the shape of that part of the container which they occupy. Liquids resist contraction even under great pressures—a result which we would expect since the molecules are now close together with little free space between them. A liquid differs from a gas mainly because the molecular attraction forces are effective and predominate over the thermal forces, having restricted the magnitude of the kinetic motion thus keeping the molecules, for the main part, within the confines of the liquid boundary. Liquids behave as if a membrane were stretched over their surfaces due to the unbalanced forces between surface molecules and liquid molecules on the lower side and vapour molecules on the upper side (a vapour has practically no attractive force). This unbalanced condition of forces at the interface of the liquid-vapour phases is manifest in the phenomena of surface tension and vapour pressure. By this view, the critical temperature takes on a new significance as being that temperature above which the molecular attraction forces no longer have an effect upon the molecules of the substance, *i.e.*, the substance no longer has a surface tension.

The escaping tendencies of a liquid are manifested by its vapour pressure and its rate of evaporation. The phenomenon of boiling is merely that condition where the internal vapour pressure of the liquid has just exceeded the external pressure acting upon the liquid (see Boiling Points, and Vapour Pressure). That the boiling point does vary with pressure can be illustrated by citing the boiling temperature and elevation of several locations. At sea level water boils at 100° C., on Mt. Mitchell, elevation 6,600 feet, water boils at 93° C., on Mt. Whitney, elevation 14,500 feet, water boils at 86° C., while on Mt. Everest, elevation 29,000 feet, water would boil at 71° C.

A liquid will absorb an amount of heat equal to its specific heat times its mass for each degree rise in temperature. When the boiling temperature is reached a much larger quantity of heat is absorbed in order to change the liquid into a gas without changing temperature. This amount of heat, called the heat of vaporization, is exactly equal in quantity and opposite in sign to the heat of condensation for a given substance. A theoretical relationship has been deduced between the vapour pressure ( $P$ ), the heat of vaporization ( $\Delta H$ ), and the absolute temperature ( $T$ ) for liquids and is called the Clausius-Clayperon equation. One useful form of this equation is :  $\log P = -\frac{\Delta H}{2.3 \times RT} + C$ , where  $R$  is the gas constant expressed in the same units as  $\Delta H$ ,  $C$  is a

constant which is a characteristic of each substance, and log is logarithm to the base 10.

When a liquid is heated its volume increases slightly, its density decreases, its vapour pressure increases, its surface tension decreases, its viscosity decreases and in general it becomes more like a gas. At the critical temperature (in a closed system) or at the boiling temperature (in an open system) the liquid changes into the gaseous state by absorbing an amount of energy equal to the heat of vaporization. This causes the kinetic energy to increase tremendously and results in the substance occupying a much larger volume and having the properties of a gas. If, on the other hand heat is removed from a liquid the volume decreases, the density increases, the viscosity increases, the vapour pressure decreases, and the surface tension increases. All these factors indicate an increase in the attraction force/thermal force ratio, which means that the molecular forces of attraction are becoming more effective and are restricting the thermal or kinetic effects of the molecules. The amount of heat removed per degree in cooling it down is equal to the specific heat times the mass of the liquid. When the freezing temperature is reached a much larger quantity of heat must be removed in order to change the liquid to the solid state without changing the temperature. This amount of heat, called the heat of crystallization, is given off when the molecules are forced to stop their translational motion and are held in a relatively fixed position by the molecular forces of attraction. The substance is now said to be in the solid state.

III. The **solid state** of matter is one in which a substance has rigidity and maintains its own shape and volume. It is a common practice to restrict the use of the term "solid state" to substances which are crystalline in character, that is, those substances which show a regularity or a symmetry in the arrangements of their atoms and molecules in the solid. Accordingly, this discussion will be about crystalline solids. The amorphous or glassy state will be mentioned later.

A crystalline solid changes to a liquid at a definite temperature, called the melting point, which has the same value as the freezing point of the liquid. For example, the freezing point of water (in the presence of nuclei—see Crystals) and the melting point of ice are both  $0^{\circ}\text{C}$ . When a solid melts it absorbs a large quantity of heat in effecting the transition from the solid to the liquid without changing the temperature. This quantity of heat, called the heat of fusion, is equal in quantity and opposite in sign to the heat of crystallization for a given substance. For example, the heat of fusion and the heat of crystallization of the water-ice system is about 80 calories per gram.

A solid such as iodine, if left open to the atmosphere at a temperature *below* its freezing point, will evaporate slowly. That is to say, it changes directly into the gaseous state without going through the liquid state, showing that solids have a vapour pressure (see same). It is common experience that solids like camphor and naphthalene (moth balls) have a vapour pressure as is evidenced by their odour.

In general the density of a solid is greater than its liquid. There

are exceptions to this, and the most common one is ice and water. Pressure has little effect upon the density of solids. Temperature likewise has slight effect upon the density of the solid state. The molecules of a solid are not to be considered thermally motionless. It is true that there is not much translational energy, but the molecules are undoubtedly vibrating about some fixed point at any temperature above absolute zero. The **atomic heat** (specific heat times atomic weight) of *solid elements* decreases to zero as the temperature approaches absolute zero and approaches a limiting value of about six calories per mole per degree as the temperature increases. This is explained by assuming that at absolute zero the forces of attraction become so strong that the individual molecules no longer vibrate independently of each other, but the whole crystal behaves like one big molecule. At higher temperatures the individual molecules begin to vibrate independently of each other and reach a limiting value when every molecule is acting as a separate vibrator (at the melting point).

The properties of a crystalline solid, such as tensile strength, elasticity, heat conductance, electrical conductance, transmission of light, and rate of solution may be different along the different axes for the same crystalline material. Such a crystal is called an **anisotropic crystal**. For example, the etching of metals develops a crystal pattern, and the colour patterns of certain crystals are produced with polarized light. Isotropic crystals show the same properties along all axis directions.

Steno in 1669 and Guglielmini in 1688 discovered that: "In all crystals of the same substance the angles between corresponding faces are the same, and are characteristic of the substance." In 1819 Mitscherlich discovered that: "Substances that are similar in chemical properties and in crystalline form should be represented by similar formulas." This means that  $\text{KH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  will crystallize out of solution on to a crystal of either  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  or  $\text{NH}_4\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ . Pasteur in 1848 was able to separate "the crystals (of sodium ammonium tartrate) which are hemihedral to the right from those hemihedral to the left, and examined their solutions separately in polarized light." He found that these two types of crystals had opposite effects upon polarized light. In 1912 Laue, Friedrich and Knipping, and Bragg developed the technique of applying X-rays to the analysis of crystalline structures. All these events agree in confirming that every solid has its own geometric form. Solids are classified into crystallographic systems based upon the geometry of the crystal (see Crystals and Crystallization).

**IV. Amorphous solids** are substances like glasses, glazes, glue, tar, gums, etc., which do not show sharp and well-defined freezing or melting points but go through a softening range. The members of this group are orphans. They are considered by some as super-cooled liquids and by others as semi-solids. The difference between the two points of view is somewhat academic. The main fact to remember is that the amorphous (glassy or vitreous) state is a condition in which certain substances can exist between the solid and liquid states.

Due to the work of Goldschmidt (1926), Zachariasen (1932), and Warren and co-workers (1933) progress has been made in elucidating the structure of the glassy state. The essential structure for this group of substances seems to be their ability to exist in a two- or three-dimensional random network lacking in periodicity, as for a liquid, but "the changes in energy and volume with temperature are similar to those of a crystalline solid" (W. Kauzmann in "Nature of the Glassy State," *Chem. Rev.*, **43**, 223 (1948)).

V. **Metastable state** is a condition of instability associated with a change from one state to another in which equilibrium has not been attained. For example, in cooling water it is possible to supercool it to  $-20^{\circ}\text{C}$ . and still have it in the liquid state; however, as soon as a crystal of ice is added the whole system solidifies and the temperature returns to  $0^{\circ}\text{C}$ . Many alloys owe their properties to this metastable state. (See Alloys, and also Colloidal State.)

VI. "**Fourth state**" — See Helium II.

*References*: *Textbook of Physical Chemistry*, by Glasstone (D. Van Nostrand Co., New York and London); *Physical Chemistry*, by Gucker and Meldrum (American Book Co., New York); *Textbook of Chemistry*, by Mack, Garrett, Haskins, Vorhoek (Ginn and Company, Boston); *Outlines of Physical Chemistry*, by Daniels (John Wiley and Sons, New York and London); *X-rays and Crystal Structure*, by W. L. and W. H. Bragg (G. Bell, London); "General Review of X-Ray Methods," by Warren (*J. App. Phys.*, **12**, 375 (1941)); *The Nature of the Chemical Bond*, by L. Pauling (Cornell Univ. Press, Ithaca); Huggins (*Chem. Rev.*, **32**, 195 (1943)); *The Modern Theory of Solids*, by F. Seitz (McGraw-Hill Book Co., New York); *The Physics of Metals*, by F. Seitz (McGraw-Hill Book Co., New York); *Phenomena at the Temperature of Liquid Helium*, by E. F. Burton et al. (Reinhold Publishing Corp., New York); *The Chemistry of Solids*, by C. H. Desch (Cornell Univ. Press).

See Atoms, Chemical Interactions, Crystals, Electrons, Elements, Nuclear Chemistry, Photons, and Radioactivity.

**MAUVEINE (Mauve)** — The first synthetic dyestuff, prepared by W. H. (later Sir William) Perkin in 1856. It is a member of the safranine group and, among other processes, it can be made by the oxidation of aniline and toluidine with potassium dichromate. It is now used to any extent only for colouring postage stamps, as the mauve colour obtained is not fast to light. (See Safranines.)

"**MAZAK**" ALLOYS — See "Zamak."

**Me** — A symbol used for methyl ( $\text{CH}_3$ ) radical.

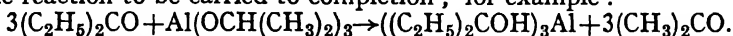
**MEASURES** — See Weights and Measures.

**MECONIC ACID** — See Opium.

**MEERSCHAUM (Sepiolite or Seafoam)** ( $2\text{MgO}, 3\text{SiO}_2, 2\text{H}_2\text{O}$ ) — A very light amorphous hydrated silicate of magnesium, of sp. gr. 0.8 to 1.0, found in certain alluvial deposits in Asia Minor, Greece, Russia, and elsewhere. As dug from the earth it is soft and soap-like, lathers with water, and is used by the Turks as a soap substitute. It is, as a rule,

slightly yellow in colour, and used also for making pipe-bowls, etc. Talc and serpentine are other varieties of magnesium silicate.

**MEERWEIN-PONNDORF REDUCTION** — A method of reducing aldehydes and ketones without affecting any other part of the molecule, and consisting in heating the carbonyl compound in benzene or toluene solution with aluminium isopropoxide, the latter becoming correspondingly oxidized to acetone, which is distilled away, thus enabling the reaction to be carried to completion; for example:



The aluminium compound of the alcohol is subsequently decomposed with dilute sulphuric acid.

**MEGA** — Prefix signifying "a million of" in the metric system.

**MELAMINE** (2,4,6-Triamino-1,3,5-triazine) is formed when dicyandiamide  $((\text{NH}_2)\text{C}:(\text{NH})\text{NH}.\text{CN})$  is heated with ammonia and methanol under pressure. Known since 1834 it became commercially available about 1940, and is used in the manufacture of melamine-formaldehyde resins which resemble urea-formaldehyde resins.

**MELDOLA'S BLUE** — An oxazine dyestuff.

**MELILITE** — The name of a group of mineral compound silicates, including *gehlenite*  $(\text{Ca}_2\text{Al}_2\text{SiO}_7)$  and *akermanite*  $(\text{Ca}_2\text{MgSi}_2\text{O}_7)$ , of crystal system No. 2, and sp. gr. about 3.0. B. E. Warren gives the formula of one variety as  $(\text{Ca}, \text{Na})_2(\text{Mg}, \text{Al})(\text{Si}, \text{Al})_2\text{O}_7$ .

**MELILOTOSIDE** — See Glycosides.

**MELINITE** — See Explosives.

**MELISSA OIL** — Obtained by distillation with water from the plant *Melissa officinalis*; of lemon odour, sp. gr. 0.894 to 0.924, opt. rot.  $0^\circ$  to  $+0.30^\circ$ , and yield 0.01 to 0.1 per cent.

**MELISSIC ACID**  $(\text{C}_{29}\text{H}_{59}.\text{COOH})$  — One of the higher members of the normal fatty acids, of m.p.  $90^\circ\text{C}$ ., and obtainable from beeswax. (See Acids.)

**MELITRIOSE** (Mellitose) — See Raffinose.

**MELLITE** — See Mellitic Acid.

**MELLITIC ACID**  $(\text{C}_{12}\text{H}_6\text{O}_{12}$  or  $\text{C}_6(\text{COOH})_6$ ) — Occurs in peat and some deposits of brown coal as so-called honeystone (mellite), or aluminium mellitate  $(\text{C}_{12}\text{Al}_2\text{O}_{12}, 18\text{H}_2\text{O})$ . When pure, it is a white, crystalline body, soluble in water and alcohol, of polybasic character, and can be obtained from lignite or graphite by oxidation with potassium permanganate.

**MELON OIL** — The seeds of the water-melon (*Citrullus vulgaris*), much cultivated in warm countries and to some extent in this country, give an oil of the semi-drying class (varying in yield from 36.8 to 48.1 per cent. on the dry seeds), having a sp. gr. of 0.9218 to 0.9236, acid value 1.3 to 17.8, ref. ind. 1.4645 to 1.467, i.v. (Hübl) 115.5 to 124.3, and sap. v. 190.1 to 195.1. The seeds are rich in protein. These figures have reference to supplies from the Kogai seed from Sierra Leone, and the Guna seed from Nigeria.

**MELONITE (Nickel Telluride)** (NiTe) — A mineral of crystal system No. 3, and sp. gr. about 5.0.

**MELTING POINTS** (See **Elements for data for individual elements, and Oxides**)—The temperatures at which fusible substances melt, or become liquid, that is, at which their solid and liquid phases are in equilibrium, and as these are affected slightly by pressure they are usually referred to normal pressure (760 mm.). It is to be noted that many mixtures, such as fats and waxes, do not solidify (freeze) until a temperature several degrees lower than their melting-points is attained. Alloys generally melt at lower temperatures than those of their components. (See **Matter**.)

**MENADIONE** — See Menaphthone.

**MENAPHTHONE (Menadione)** ( $C_{11}H_8O_2$ ) — A bright yellow, crystalline compound, namely, 2-methyl-1,4-naphthaquinone, prepared by oxidation of 2-methylnaphthalene; insoluble in water; slightly soluble in alcohol and in fixed oils; m.p.  $105^\circ$  to  $107^\circ$  C. It has the physiological action of vitamin K and is administered by injection for the prevention of neonatal hæmorrhage and for other hæmorrhagic conditions. (See **Acetomenaphthone**, and **Vitamins (vitamin K)**.)

**MENDELEEFF'S PERIODIC ARRANGEMENT** — See **Elements**.

**MENHADEN OIL** — See **Fish Oils**.

**MENISCUS** — The curved surface of a liquid confined in a tube due to capillarity, as shown by a solution contained in a burette or by the column of mercury in a barometer; concave when the liquid wets the container, as with water, otherwise convex, as with mercury.

**MENSTRUUM** — Any solvent liquid used for extracting the soluble parts of a material.

**MENTHENE** ( $C_{10}H_{18}$ ) — A hydrocarbon—6 possible isomers—which possesses one olefine bond and the carbon skeleton of cymene.  $\Delta^3$ -Menthene ( $CH_3.C_6H_8.CH(CH_3)_2$  (1, 4)) occurs in oil of thyme, has the odour of cymene, and b.p.  $168^\circ$  C. It is obtained from menthol by the elimination of water or from menthyl chloride by the removal of hydrogen chloride.

**MENTHOL** ( $C_{10}H_{19}OH$ ) — A colourless, crystalline, secondary alcohol obtained from the volatile oils of various species of *Mentha* or prepared synthetically. It occurs in the form of prismatic crystals having a pungent odour and warm and aromatic taste; m.p.  $42^\circ$  to  $44^\circ$  C. (natural lævo-menthol),  $32.5^\circ$  to  $34^\circ$  C. (synthetic racemic menthol); opt. rot.  $-49^\circ$  to  $-50^\circ$  (natural menthol); b.p. about  $212^\circ$  C.; sp. gr. about 0.890 at  $15^\circ$  C.; soluble in alcohol, ether, chloroform, and essential oils. It can be prepared from piperitone and thymol by hydrogenation. It is used in medicine and perfumery. A method for the production of menthol from the terpenes of peppermint oil is described in a U.S.S.R. patent (No. 65823). (See *Drug and Cosmetic Industry*, 61, 684 (1947).)

**MENTHONE** ( $C_{10}H_{18}O$ ) is a ketone related to menthol ( $C_{10}H_{19}OH$ ), and occurs with that substance as a constituent of oil of peppermint; both it and menthol can be produced chemically from the oil of *Eucalyptus dives* and *E. piperita*. It boils at  $207^{\circ}C.$ , is of sp. gr. 0.896, and is easily converted into thymol. According to S. Komatsu, and M. Kurata, when *l*-menthone is passed slowly through a glass or silica tube at  $300^{\circ}C.$  in presence of copper acting as a catalyst, it yields 70 per cent. thymol, 22 per cent. cymene, and 3 per cent. menthene. (See Ogata (*J.S.C.I. Japan*, **45**, 428 B (1942); and Thymol.)

**MEPACRINE HYDROCHLORIDE** ("Atabrine," "Atebrin," Quinacrine Hydrochloride) ( $C_{23}H_{30}ON_3Cl \cdot 2HCl$ ) — The dihydrochloride of 3-chloro-7-methoxy-9-(1-methyl-4-diethylaminobutylamino)-acridine; a yellow crystalline powder, soluble about 1 in 30 water and in alcohol. The methanesulphonate ("Atebrin Musonat") is also used and is soluble 1 in 3 of water and 1 in 36 of alcohol (95 per cent.).

Mepacrine is a synthetic substitute for quinine in the treatment of malaria. It was introduced in 1930, and by the end of 1942 the rate of production in the United States was said to be sufficient to treat more than 50,000,000 cases of malaria, a production equivalent to the total pre-World War II supply of quinine. (See "Chemistry and Development of Atabrine and Plasmochin," by A. E. Sherndal in *Chem. Eng. News*, **21**, 1154 (1943); "Fighting the Malaria Germ" in *Discovery*, **6**, 78 (1945); and "Quinacrine Hydrochloride," by R. G. Jones and others in *Ind. Eng. Chem.*, **37**, 1044 (1945).)

**MEPERIDINE HYDROCHLORIDE** — See Pethidine Hydrochloride.

**MERCAPTALS (Thioacetals)** — Sulphur compounds being analogues of acetals, such as  $CH_3CH(SC_2H_5)_2$ . (See Acetals.)

**MERCAPTANS (Thioalcohols)** — A group of liquid, inflammable, organic compounds containing the SH group, analogous to the monohydric alcohols. They have a very sharp, unpleasant (garlic-like) odour, are insoluble in water, but soluble in alcohol. Their relationship to alcohol is shown by the two illustrative formulas:  $C_2H_5OH$  (ethyl alcohol),  $C_2H_5SH$  (ethyl thioalcohol). They may be prepared by several methods; for example, by heating ethyl alcohol with phosphorus pentasulphide, the oxygen being thus replaced by sulphur, or by heating a mixture of an alkyl halide with potassium hydrosulphide.

The thioethers or dialkyl sulphides, such as ethyl sulphide,  $(C_2H_5)_2S$ , are neutral volatile liquids devoid of acid character.

**MERCAPTIDES** — Metallic derivatives of mercaptans in which hydrogen of the SH group is replaced by a metal. As mercaptans are more acidic than the corresponding alcohols, the mercaptides are more stable than the metallic alkoxides.

**MERCERIZATION** — See Cellulose, and Silk Substitutes.

"**MERCEROL**" — See Wetting Agents.

**MERCUROCHROME** ( $C_{20}H_8O_6Br_2Na_2Hg$ ) — A dark red phthalein dye, being the disodium salt of dibromohydroxymercurifluorescein. It occurs in the form of greenish, lustrous granules which yield a deep red solution having a distinct green fluorescence; readily soluble in water; almost insoluble in alcohol; insoluble in ether. It possesses weakly bactericidal properties and has a more powerful antiseptic action in acid media.

**MERCURY** (*Hydrargyrum*, *Quicksilver*) (Hg) and its Compounds — Atomic weight, 200.61. See Elements for other data. Mercury occurs in nature to some extent in the free or globular state admixed with its ores (particularly the sulphide), of which *cinnabar* ( $HgS$ ) is the best known; also in the mineral *turpeth* as a basic sulphate ( $Hg_3SO_6$  or  $HgSO_4 \cdot 2H_2O$ ). Supplies of mercury ores occur in Algeria, Austria, Italy, Mexico, New Zealand, Spain, California, Nevada, Oregon, Washington, China, Chile, Japan, etc.

The metal is made from the natural sulphide by roasting the ore, whereby the sulphur is burnt off as sulphur dioxide, or by heating the ore mixed with lime in closed retorts. In this last-named process the lime combines with the sulphur, whilst the mercury is liberated and distils over as vapour, which is then condensed. In the "Thornhill" process of extraction, the natural sulphide is dissolved in a 4 per cent. solution of sodium sulphide and 1 per cent. caustic soda, and the mercury is precipitated therefrom by aluminium turnings.

Mercury is a bright, silver-coloured, liquid metal which solidifies in crystal system No. 1 upon cooling and melts at  $-38.9^\circ C.$ ; assumes a crystalline (rhomboidal) structure at  $-80^\circ C.$ , and readily combines with many other metals, forming alloys or combinations which are called *amalgams*. Its vapour and all its compounds are poisonous, and cases of poisoning have been attributed to silver-amalgam dental fillings.

There are several isotopes of mercury, and their partial separation can be effected by evaporating the metal at low pressure and condensing the evaporated atoms on a cooled surface, the density of the condensed mercury being slightly lower than that of the residual metal.

Apart from its uses in the construction of thermometers and barometers, it is used in making mirrors, amalgams, extraction of gold from its ores, the manufacture of vermilion, in various electrical applications, in the generation of power in the mercury-steam boiler, and in the preparation of mercury compounds.

**Oxides** — When submitted to long heating in the air somewhat above  $300^\circ C.$ , mercury is slowly converted into the red mercuric oxide ( $HgO$ ), and when this oxide is heated to redness (temperature well above  $300^\circ C.$ ) it is again decomposed into its constituent elements. The red oxide is used as a pigment and for making anti-fouling marine paints. The yellow variety, as obtained by precipitation from a mercuric solution by sodium hydroxide, is stated to have the same crystalline form as the red variety and differing from it in the smaller size of the yellow oxide particles, and is also used as a pigment.

## MERCURY

## MERCURY METAL, WORLD PRODUCTION

Annual average for the three-year period 1937-1939  
Data arranged and rounded off by the Editor.

Country	Metric Tons
Italy .. .. .	2,310
Spain .. .. .	1,210
Czechoslovakia .. .. .	100
	<hr/>
	3,620
U.S.S.R. .. .. .	300
U.S.A. .. .. .	610
Mexico .. .. .	240
	<hr/>
	850
Sum of above .. .. .	4,770

WORLD PRODUCTION, approximately the above.

Production of mercury metal in Canada during World War II was noteworthy, namely, in 1941, 240 metric tons ; 1942, 470 ; 1943, 770 ; 1944, 330.

The lower oxide ( $\text{Hg}_2\text{O}$ ) is precipitated in a dark brown form when sodium hydroxide is added to a mercurous salt in solution ; it is unstable, and when exposed to light or gently heated it is converted into mercury and the higher oxide.

The *salts* of mercury corresponding to the lower oxide ( $\text{Hg}_2\text{O}$ ) are styled "mercurous," while those corresponding to the higher oxide ( $\text{HgO}$ ) are classified as "mercuric" compounds.

**Mercurous Chloride** (*calomel*) ( $\text{Hg}_2\text{Cl}_2$ ) is a white, crystalline body, insoluble in water, used in medicine. It is found in native form as horn-mercury (*horn-quicksilver*).

**Mercurous Nitrate** ( $\text{Hg}_2(\text{NO}_3)_2$ ) can be obtained in colourless monosymmetric crystalline form (containing two molecules of associated water). It is soluble in water acidified with cold dilute nitric acid, but is not very stable in character.

**Mercurous Sulphate** ( $\text{Hg}_2\text{SO}_4$ ) is a white, crystalline compound very slightly soluble in water.

**Mercuric Chloride** (*corrosive sublimate*) ( $\text{HgCl}_2$ ), is a white, crystalline poisonous substance, soluble in water, and of powerful germicidal character, for which reason it is used as a wood preservative, also by taxidermists in preparing the skins of animals, and by surgeons (in dilute solutions) as an antiseptic wash, etc. It melts at  $277^\circ\text{C}$ . and boils at  $303^\circ\text{C}$ ., and readily forms double salts, which are more soluble than mercuric chloride, *e.g.*,  $\text{HgCl}_2 \cdot \text{HCl}$ . Stannous chloride ( $\text{SnCl}_2$ ) reacts with mercuric chloride to form mercurous chloride ( $\text{HgCl}$ ), white precipitate, and sometimes also mercury ( $\text{Hg}$ ), black precipitate.

Aminomercuric chloride ( $\text{NH}_2\text{HgCl}$ ), "infusible white precipitate" and diamino mercuric chloride ( $(\text{NH}_2)_2\text{HgCl}_2$ ), "fusible white precipitate" are formed by reaction with ammonium hydroxide. Relation:  $\text{NH}_2\text{HgCl} + \text{NH}_4\text{Cl} \rightleftharpoons (\text{NH}_2)_2\text{HgCl}_2$ .

**Mercuric Sulphate** ( $\text{HgSO}_4$ ) is a white, crystalline substance, insoluble in water, used in the preparation of the two chlorides and in the extraction of gold and silver from roasted pyrite.

**Mercuric Iodide** ( $\text{HgI}_2$ ) is insoluble in water and is dimorphous; when heated to  $150^\circ\text{C}$ . the scarlet tetragonal crystals are changed into another and yellow rhombic crystalline form, but upon cooling and being lightly touched is at once retransformed into the original state.

**Mercuric Nitrate** ( $\text{Hg}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ) is a crystalline, deliquescent soluble salt used in medicine and felt manufacture. (See Millon's Test.)

**Mercuric Sulphide** ( $\text{HgS}$ ), as obtained by the precipitation of a mercuric salt with hydrogen sulphide, is ultimately black, although it passes through the colour stages of white, yellow, red, and brown on the way, and when washed, dried, and sublimated, it becomes red, forming the so-called "vermilion," in which form it is manufactured for use as a pigment and for colouring sealing-wax (red). The native sulphide (cinnabar) and the artificially prepared form (vermilion) are bright red.

**Mercuric Thiocyanate** ( $\text{Hg}(\text{SCN})_2$ ) is a white, poisonous, and explosive body used in preparing so-called "Pharaoh's serpents" and in photography.

**Mercuric Cyanide** ( $\text{Hg}(\text{CN})_2$ ) is colourless, crystalline, soluble in water, and used for making cyanogen gas and in photography.

**Mercury Fulminate** — See Fulminating Mercury.

**MERCURY BOILER** — See Steam.

**MERCURY LAMP** — An electric light of a few definite frequencies, produced by passing an electric current through mercury vapour, used for illumination and one of the richest sources of ultra-violet radiation when the mercury is confined in a quartz tube. (See E. J. Bowen on "Light Filters for the Mercury Lamp" (*J.C.S.*, 1932, 2236); Fluorescence, and Ultra-Violet Rays.)

"**MERFENIL**" — See Phenylmercuric Nitrate.

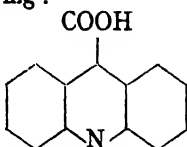
**MERSALYL** ("Salyrgan") ( $\text{C}_{13}\text{H}_{16}\text{O}_6\text{NNaHg}$ ) — A white, odourless, deliquescent compound being the sodium salt of salicyl-( $\gamma$ -hydroxymercuri- $\beta$ -methoxypropyl) amide-*o*-acetic acid, containing about 39.5 per cent. of mercury; very soluble in water; soluble in alcohol; insoluble in ether and chloroform. It has a powerful diuretic action and is administered by injection for this purpose. Solutions for injection contain theophylline to prevent decomposition of mersalyl which may, otherwise, become toxic.

**MERTHIOLATE** — See Thiomersolate.

**MESITYLENE** — See Hydrocarbons (Benzene).

**MESO** — A prefix used to distinguish certain stereoisomeric forms, e.g., mesotartaric acid, optically inactive because of internal compensation; and to describe the position of a group in a molecule, when that group is centrally placed. For example, the following compound is known K.C.E.—22

as acridinemesocarboxylic acid, the name denoting that the COOH radical is on the central ring :



Meso is applicable to the 9 and 10 positions of anthracene derivatives.

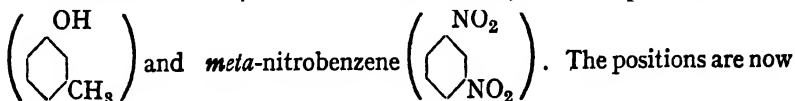
**MESON** — Highly energetic cosmic rays acting on the walls of the cloud chamber cause the ejection of mesons. Predicted by Yukawa, and discovered by Carl Anderson in 1936. Mesons are artificially made by shooting 380-million-electron-volt alpha particles into a beryllium or carbon target. They are sub-atomic particles of very short life, namely,  $10^{-6}$  second, having a mass approximately 200 times that of the electron, and unit charge positive or negative. Several different types of mesons are known with at least two different masses. Mesons are instrumental in nuclear binding.

**MESULPHEN** (Dimethylthianthrene, Dimethyldiphenylene Disulphide, "Mitigal," "Sudermo") ( $C_{14}H_{12}S_2$ ) — A yellow, oily liquid consisting mainly of 2,6-dimethylthianthrene ( $CH_3.C_6H_3.S_2.C_6H_3.CH_3$ ) and having a slight but not unpleasant odour; insoluble in water; soluble in ether, chloroform, and acetone. It is used in medicine for the treatment of scabies, acne and other skin diseases.

**MESOTHORIUM** — See Thorium.

"**META**" (Metaldehyde) ( $C_2H_4O$ )<sub>n</sub> is a white, crystalline substance which can be used as a solid fuel and might possibly replace denatured alcohol. It is clean and free from danger, and is produced by the polymerization of acetaldehyde. The latter may be polymerized into two compounds, namely, paraldehyde, which is a harmless and efficient mild hypnotic of b.p.  $124^\circ$  C. and soluble in water, and metaldehyde, which sublimates at about  $112^\circ$  C. and is insoluble in water. Acetaldehyde is treated with a trace of concentrated sulphuric acid, whereupon paraldehyde is formed accompanied by the evolution of heat and a contraction in volume. When acetaldehyde is condensed and treated in cast-iron vessels at  $15^\circ$  C. with sulphuric acid (as a catalyst), metaldehyde is precipitated. The heating value of the compressed compound is 6,136 calories per kilo as against 7,065 per kilo, or 5,162 calories per litre of alcohol.

**META COMPOUNDS** are substitution products derived from benzene in which the substituting radicals or groups are constitutionally situated in certain definite positions on the nucleus, for example, *meta*-cresol



The positions are now more commonly expressed numerically, for example, 1,3-dinitrobenzene for the latter substance, and 3-methylphenol for the former. (See Benzene Ring.)

**META-CRESOL** — See Cresol.

**META-NITRANILINE** ( $C_6H_4(NO_2)(NH_2)$  (1, 3)) — A yellow crystalline intermediate, soluble in alcohol and ether.

**META-PHENYLENEDIAMINE** ( $C_6H_4(NH_2)_2$  (1, 3)) — A colourless, crystalline intermediate, soluble in water, alcohol, and ether.

**METAPROTEINS** — Early products of the hydrolysis of proteins, retaining many of their characters but not coagulable by heating.

**METASTANNIC ACID** — See Tin Compounds.

**META-TOLYLENEDIAMINE** — See Tolylenediamine.

**METABOLISM** — The various changes affecting the tissues of the body and energy resulting from the conversion of food in living organisms.

**METALLIC CARBONYLS** — Volatile compounds of metals with carbon monoxide: the orange cobalt compound  $(Co(CO)_4)_2$  passing into jet black  $(Co(CO)_3)_4$ ; the colourless liquid nickel carbonyl  $Ni(CO)_4$  of b.p.  $43^\circ C$ . The carbonyls of chromium, molybdenum and tungsten are colourless, orthorhombic crystals of general formula  $M(CO)_6$ . These are relatively stable, the vapour decomposing slowly only above  $120^\circ C$ . Ruthenium at  $180^\circ C$ . and 200 atmospheres' pressure yields white, crystalline pentacarbonyl  $Ru(CO)_5$ , of m.p.  $-22^\circ C$ ., from which orange yellow crystals of  $Ru_2(CO)_9$  can be prepared, only decomposing at  $200^\circ C$ . in the absence of air. The iron carbonyl  $(Fe(CO)_5)$  is a yellow, viscid, poisonous liquid, of b.p.  $103^\circ C$ .; it is soluble in benzol, and can be used as an anti-knock agent in liquid fuels for internal combustion engines. Other compounds include the compositions  $Fe_2(CO)_9$  and  $Fe(CO)_4$ . The vapours of metallic carbonyls are poisonous. (See *Ann. Rep. Prog. Chem.*, 33, 176 (1936).)

**METALLIC ORGANIC COMPOUNDS** — See Organo-Metallic Compounds.

**METALLIC SOAPS** — See Soaps.

**METALLISATION** — See Metals.

**METALLOGRAPHY** — A division of metallurgy dealing specifically with the study of the intrinsic nature of metals and alloys with respect to their chemical and physical behaviours. While optical methods constitute an important phase of this study, other physical techniques are also employed, such as thermal hardness, X-ray, magnetic, and electrical analyses.

*References:* *The Principles of Metallographic Laboratory Practice*, by G. L. Kehl (McGraw-Hill Book Co., New York); *The Physical Examination of Metals*, Vols. I and II, by B. Chalmers and A. G. Quarrell (Longmans, Green and Co., New York); *A Text Book of Metallography*, by G. Tammann (Reinhold Publishing Corp., New York); *Principles of Metallography*, by R. S. Williams and V. O. Homerberg (McGraw-Hill Book Co., New York); *Metallography*, Vols. I and II, by S. L. Hoyt (McGraw-Hill Book Co., New York); *Physical Metallography*, E. Heyn and M. A. Grossmann (John Wiley and Sons, New York); *Metallography of Aluminium Alloys*, by L. F. Mondolfo (John Wiley and Sons, New York); *The Metallography of Steel and Cast Iron*, by H. M. Howe (McGraw-Hill Book Co., New

York); *The Metallography and Heat Treatment of Iron and Steel*, by A. Sauver (McGraw-Hill Book Co., New York); *The Metallography of Iron and Steels*, by C. H. Plant (Sir Isaac Pitman and Sons, London).

**METALLOID** — A term applied to those elements, such as arsenic and selenium, which are not decidedly metallic, but occupy a position on the borderland between the absolutely metallic and non-metallic elements.

**METALLURGY** — A science devoted to the extraction of metals from ores, and to the production of metals and alloys for useful purposes. This science is divided into three important divisions, namely, process metallurgy, metallography, and physical metallurgy. There is a trend toward further subdivisions because of expansion and specialization. For further information, see references under each of the above divisions.

**METALS** — The metallic elements as a class are capable of taking a high polish: gold, copper, and platinum may be polished and burnished to a very high degree, much more than iron, lead, and arsenic. Some are much more *ductile* than others, and can therefore be easily drawn out into wire; copper and aluminium in this form are largely used for electrical conductors. Some are of a *malleable* character, that is to say, can be easily beaten into any desired shape, for example, lead, while gold and several other metals can be hammered into extremely thin sheets, such as gold leaf, for example. (See Gold.)

Most metals are good *conductors* of heat, sound, and electricity, and at a temperature approaching absolute zero, pure metals lose practically all electrical resistance and become nearly perfect conductors.

Some metals combine by diffusion and solid masses can be obtained under pressure, as in the making of tungsten wire from the powder form.

There are great differences between the hardness, brittleness, weight, tensile strength, and other properties of the various metals, and it has been demonstrated that the corrosion of metals is mainly, and probably entirely, due to electrochemical changes.

Hardness, density, melting-point, and electrical conduction data are displayed in the table in the article on Elements. Data on the ultimate strength of some metals and alloys will be found under Strength (Tensile). The output of principal metals and their ores for eight countries is presented under Economic Aspects, and for most metals of commercial importance under each metal.

*References*: McMyn and Edge on "Acid-Resisting Metals" (*Chem. and Ind.*, **50**, 474 (1931)); "Atmospheric Corrosion of Metals," by J. C. Hudson (3rd Report to Atmospheric Corrosion Research Committee, with discussion, *Faraday Society*, May 23, 1929), and by W. H. J. Vernon (*Transactions of the Faraday Soc.*, No. 121, **27**, part 6, June, 1931); *The Corrosion of Metals*, by U. R. Evans (E. Arnold and Co., London); "Resistant Metals," by C. R. Vincent (*Ind. Eng. Chem.*, **29**, 289 (1937)); *The Structure of Metals and Alloys*, by W. Hume-Rothery (Institute of Metals, London); *Atomic Theory for Students of Metallurgy*, by W. Hume-Rothery (Institute of Metals, London); *An Introduction to the Electron Theory of Metals*, by G. V.

Raynor (Institute of Metals, London); *The Physical Structure of Alloys*, by C. E. Beynon (Edward Arnold and Co., London); *Structure of Metals*, by C. S. Barrett (McGraw-Hill Book Co., New York); *The Physics of Metals*, by F. Seitz (McGraw-Hill Book Co., New York); *The Theory of the Properties of Metals and Alloys*, by N. F. Mott and H. Jones (Clarendon Press, Oxford); *Metals*, by Sir Harold Carpenter and J. M. Robertson (Oxford University Press); *Metals Reference Book*, by C. J. Smithells (Interscience Publishers, New York); *Conference on the Fatigue and Fracture of Metals*, Massachusetts Institute of Technology, Cambridge, Massachusetts, June 19–22, 1950; *Symposium on the Failure of Metals by Fatigue*, Melbourne (Australia) University Press, 1947; *Fracturing of Metals*, American Society for Metals, Cleveland, Ohio, 1948; *Fracture of Metals*, American Welding Society, New York, 1947; "Cold Working of Metals" (*Trans. Amer. Soc. Metals*, **41A** (1949)); also Alloys, Brinell's Ball Test, Corrosion, Hardness, and Ores.

**Colouring of Metals** can be produced by many chemical methods using various reagents, and by electrical means, such as the deposition of copper upon iron or zinc surfaces by immersion in a dilute solution of cupric sulphate. Again, pickled zinc, when immersed in a dilute solution of copper tartrate and caustic soda, assumes a colouring (from violet to purple-red) which can be arrested at any stage. By heating metals to various temperatures, the surfaces of many can be coloured by oxidation, a greater range of colouring being realized by first of all treating them with various chemical reagents. These temper colours are possibly due to interference of light reflected in a similar manner to Newton's rings from the two surfaces of a film of a surface compound. (See *Chemical Colouring of Metals*, by S. Field and S. R. Bonney (Chapman and Hall, London).)

Gun-barrels are bronzed by rusting of the barrels while the ends are plugged, the rust being converted into magnetic oxide by boiling in water through which air is passing. The commoner bronzing of gun-barrels is done with compounds of antimony. Iron, steel, and cast-iron articles can be made dull black by electrically treating them in a caustic soda solution, whereby a sodium ferrate solution is obtained and a coating of magnetic oxide results, which is not capable of absorbing oxygen, although the articles are not thus rendered entirely rust-proof. It has been pointed out by J. D. Bengough and H. Sutton that the resistance of aluminium to corrosion due to the presence of a protective film of oxide can be greatly increased by anodic oxidation and the anodic layer can be coloured almost as desired.

See "Some Properties of Protective Films on Metals," by E. S. Hedges (*Chem. and Ind.*, **50**, 21, 768 (1931)); *Metals and Alloys Data Book*, by S. L. Hoyt (Reinhold Publishing Corp., New York); *The Science of Metals*, by Zay Jeffries and R. S. Archer (McGraw-Hill Book Co., New York); *Protective Coatings for Metals*, by R. M. Burns and A. E. Schuh (Reinhold Publishing Corp., New York); Copper, Corrosion, Electro-plating, Paints, and Rustless Iron and Steel.

**Metal Spraying** — A process of metal spraying is as follows: A wiring of the metal is pulled into a pistol fed with oxygen and a combustible

gas under pressure, and also with compressed air, and in this way minute particles of the wiring are projected from the melting end in the form of spray. Any metal obtainable in wire form and fusible in the oxyhydrogen flame can be used for spraying on to surfaces of paper, stone, concrete, porcelain, leather, celluloid, and various fabrics, wood, or metal. Metal surfaces to be thus coated are first of all roughened by a sand-blast to ensure adhesion, and coatings of any desired thickness greater than 0.02 mm. may be made, 0.05 generally sufficing for rust prevention. The surface thus produced is always matte, but may be polished, if desired, and is a good one for paints. Metal dust or powder can also be used in another apparatus, and any non-ferrous metal may be applied to a ferrous metal, or *vice versa*. A method for producing homogeneous lead linings of somewhat similar character has been recently developed, a lead wire being melted and atomized by means of a pistol charged with carbon-dioxide heated to 350° to 400° C.

The process is employed for the protection of certain portions of ships and propellers; among other applications, for the zincing of rail-ends and fish-plates, and for connecting purposes on electric railways, thus obviating the necessity for copper connections and continual cleaning.

**Metal Pickling** — See Galvanizing.

**Metal Recovery** from waste materials. (See Waste Products.)

**"Sherardizing"** or vapour galvanizing, is said to be best effected by heating the subject-metal with zinc dust in a closed vessel at about 370° to 380° C. (which is below the melting-point of zinc, 419° C.) for about half an hour, thus producing in respect of iron an 8 Fe-92 Zn alloy penetrating to a depth of about 0.002 in. and imparting to the metal great resistance to corrosion. When it is specified that the work is to pass the "Preece" test for corrosion (immersion in solution of copper sulphate without the deposition of bright copper), a thin layer of pure zinc must be built up above the surface of the original metal. The zinc dust can be replaced by zinc-iron alloy FeZn<sub>10</sub>.

The general process is applicable to iron and many other metals, and used in respect of small articles such as frames, table-tops, panels, trays, vases, electric-light fittings, etc. In Schoop's process the metal is sprayed over the subject body to be coated at a high velocity.

**"Calorizing"** is really a development of "sherardizing," and is a process for the surface impregnation of steel, iron, copper, brass, nickel, etc., with aluminium, thus forming a homogeneous alloy to a certain depth. This is ordinarily effected by placing the subject metal in an air-tight retort charged with a mixture of finely divided aluminium and alumina, and heating to from 900° to 1,000° C. in a reducing current of hydrogen. The alloy thus produced is rich in aluminium, and on subjection to high temperatures under working conditions, the aluminium penetrates or diffuses through into the metal, an outer coating of aluminium oxide forming a protective surface. It is alleged that the homogeneous alloy will resist oxidation up to 1,800° F. (982.2° C.). The "Meker" process employs coatings with powdered Al<sub>3</sub>Fe mixed with about 0.7 per cent. of aluminium chloride and heat treatment, and is stated to give more satisfactory results.

Calorized non-ferrous metals, such as brass, copper, and nickel, are excellent non-corrosive materials, resistant to oxidation at high temperatures and to acid liquors.

**Powder Metallurgy** — See same.

(See Corrosion, Diffusion, Passivity, and Welding.)

**METAMERIC** — Substances which have the same molecular weights and identical percentage composition, but are of different types, properties, and structure, and furnish different products by chemical changes—for example, acetone  $((\text{CH}_3)_2\text{CO})$ , and allyl alcohol  $(\text{C}_3\text{H}_5\text{OH})$ . (See Isomerism.)

**METAMORPHISM** — The changes in minerals (rocks) of their chemical and physical characters under the influences of heat, pressure, and chemical interaction.

**METASTABILITY** — See Matter.

**METEORITES** — Mineral substances (aerolites) of meteoric origin which have fallen on the earth's surface, some of iron or iron alloyed with nickel ; many others are composed of silicates or of the various elements entering into the composition of terrestrial minerals. Most of them are fused on their surfaces, doubtless brought about by the high temperature induced by their rapid passage through the atmosphere. About one-half of the meteorites that enter the earth's atmosphere have velocities less than 26 miles per second, and the other half have greater velocities. Furthermore, the average height of the middle of a meteor trail is about 55 miles, which is the same height as that of the ionosphere which reflects radio waves.

**METER** — See Weights and Measures.

**METERS** — Instruments for measuring quantities of materials, especially liquids and gases ; and of energy, especially electrical current and potential. (See Recorders.)

" **METHACROL** " (Du Pont) — Trade-mark for a series of dispersions of a thermoplastic resin, used as a base for finishing nylon, silk, and leather.

**METHACRYLATE POLYMERS** (Du Pont)  $(\text{CH}_2 : \text{C}(\text{CH}_3).\text{COOR})_n$  ; where R is ethyl, *n*-butyl, isobutyl, *n*-butyl-isobutyl, and the polymer is a clear, colourless, thermoplastic resin. Used in coating compositions, adhesives, textile finishes, and wax tougheners.

" **METHADON** " — See Amidone.

**METHANE** — See Hydrocarbons (Methane).

**METHANOL** — See Alcohols (Methyl).

" **METHEDRINE** " — See Methylamphetamine.

" **METHOXYCHLOR** " — An analogue of D.D.T. having the chemical formula  $(\text{CH}_3\text{OC}_6\text{H}_4)_2\text{CHCCl}_3$  and named 2,2-*bis*(*p*-methoxyphenyl)-1,1,1-trichloroethane, said to be more efficient than D.D.T. against certain insects, and of low toxicity to warm-blooded animals. (See Prill, *et al.* (*Science*, **101**, 464, (1951)) ; and Insecticides.)

**METHYL** — The monovalent (univalent) radical  $\text{CH}_3$ ; to add to or substitute which in a compound is termed "methylation." (See Radicals.)

**METHYL ACETATE** — See Esters.

**METHYL ACETOACETATE** ( $\text{CH}_3\text{COCH}_2\text{COOCH}_3$ ) — A colourless liquid, b.p.  $170^\circ\text{C}$ ., d. 1.077, is the lowest molecular weight acetoacetate. In synthesis it can be made to function as ester, ketone, or alcohol.

**METHYL ALCOHOL** (Methanol) — See Alcohols (Methyl).

**METHYLAMINE** — See Amines.

**METHYLAMPHETAMINE** (Methedrine) ( $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{CH}(\text{NH}\cdot\text{CH}_3)\cdot\text{CH}_3$ ) — A colourless liquid; sparingly soluble in water, miscible with alcohol, chloroform, and ether; b.p.  $212^\circ$  to  $215^\circ\text{C}$ . It is used in inhalers as a local vaso-constrictor for the relief of nasal congestion. The hydrochloride is a white crystalline powder, soluble in water; m.p.  $172^\circ$  to  $174^\circ\text{C}$ .; used in medicine as a stimulant.

**METHYL-*n*-AMYL KETONE** ( $\text{CH}_3\cdot\text{CO}\cdot\text{C}_5\text{H}_{11}$ ) boils at  $151^\circ\text{C}$ ., and is used as a lacquer solvent.

**METHYL ANTHRANILATE** — See Neroli Oil.

**METHYL BENZOATE** (Essence Niobe) — See Esters.

**METHYL BLUE** — See Aniline, and Dimethylaniline.

**METHYL BROMIDE** ( $\text{CH}_3\text{Br}$ ) — A colourless volatile liquid of sp. gr. 1.732, b.p.  $4\cdot6^\circ\text{C}$ .; soluble in alcohol and ether; prepared by action of bromine on methyl alcohol in presence of phosphorus, followed by distillation; used for rendering ethyl and methyl chlorides non-flammable.

**METHYL CHLORIDE** (Chloromethane) ( $\text{CH}_3\text{Cl}$ ) — A colourless gas of ethereal odour and b.p.  $-23\cdot7^\circ\text{C}$ .; used in medicine, the extraction of perfumes from flowers, and for refrigeration; prepared among other methods by the action of hydrochloric acid gas on warm methyl alcohol containing half its weight of zinc chloride in solution. It is soluble in water and alcohol and can be rendered non-flammable by suitable admixture with methyl bromide. (See "Artic.")

**METHYL CINNAMATE** ( $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CH}\cdot\text{COOCH}_3$ ) occurs in varying balsamic products, and is prepared from cinnamic acid and methyl alcohol in the presence of sulphuric acid, followed by distillation. It is a colourless crystalline substance, of m.p.  $33^\circ\text{C}$ ., b.p.  $263^\circ\text{C}$ .; soluble in alcohol and ether, and used for flavouring and in perfumery.

**METHYL ETHER** — See Ethers. Some methyl ethers are listed under Monomethyl Ether of each.

**METHYLETHYL KETONE** (2-Butanone) ( $\text{CH}_3\cdot\text{CO}\cdot\text{C}_2\text{H}_5$ ) — A colourless liquid, of sp. gr. 0.805 and b.p.  $79\cdot6^\circ\text{C}$ .; formed by oxidation of secondary butyl alcohol, and used in making smokeless gunpowder.

**METHYL IODIDE** ( $\text{CH}_3\text{I}$ ) — A colourless liquid, of sp. gr. 2.279 and b.p.  $42.5^\circ\text{C}$ ., prepared by interaction of methyl alcohol, sodium iodide, and sulphuric acid, followed by distillation. It is an important methylating agent in organic chemistry, and is used in cases where the more destructive dimethylsulphate would injure the compound being methylated.

**METHYL SALICYLATE** (Artificial Oil of Wintergreen) ( $\text{C}_6\text{H}_4(\text{OH})\text{COOCH}_3$  (1, 2)) — The principal constituent of oil of wintergreen. A colourless liquid, of sp. gr. 1.184 and b.p.  $223.3^\circ\text{C}$ ., soluble in alcohol and ether. Chemically, it is the methyl ester of salicylic acid, and is prepared by heating a mixture of methyl alcohol and salicylic acid in presence of sulphuric acid, followed by distillation. It is used in medicine and for flavouring purposes. (See Gaultheria Oil.)

**METHYL VIOLET** — A synthetic dye. (See Crystal Violet, and Aniline.)

**METHYLAMINE** — See Amines.

**METHYLATED SPIRITS** — Ethyl alcohol to which wood naphtha and other authorized substances have been added to render it unfit for human consumption. Denatured alcohols are of the following types :

*Industrial Methylated Spirit* consists of 19 volumes of ethyl alcohol (95 per cent.) and one volume of approved wood naphtha. This strength is known as "66 O.P. Industrial Methylated Spirits." It can also be obtained in a strength corresponding to 74 O.P. which is known as "Absolute Industrial Methylated Spirit."

*Industrial Methylated Spirit (Pyridinized)* consists of Industrial Methylated Spirit containing 0.5 volume of crude pyridine to every 100 volumes.

*Mineralized Methylated Spirit* consists of 90 volumes of ethyl alcohol (95 per cent.), 9.5 volumes of wood naphtha, and 0.5 volume of crude pyridine ; in addition 0.375 gallon of mineral naphtha (petroleum oil) and 0.025 oz. of powdered aniline dye (methyl violet) are added to each 100 gallons.

For the legal requirements governing the sale and use of methylated spirits in the United Kingdom see *The Methylated Spirits Regulations* (H.M.S.O.), and in the United States, *Regulations for the Use of Denatured Alcohol*, issued by the Treasury Department, Washington, D.C.

**METHYLATION** — See Methyl.

**METHYLENE** — The divalent radical  $\text{>CH}_2$ , and the hypothetical first member of the olefine series of hydrocarbons.

**METHYLENE BLUE** ( $\text{C}_{16}\text{H}_{18}\text{N}_3\text{ClS}\cdot 3\text{H}_2\text{O}$ ) — A blue thiazine dye, namely, tetramethylthionine chloride, occurring as a dark greenish crystalline powder having a metallic lustre ; soluble in water, alcohol and chloroform. It is used in medicine, in volumetric analysis as an oxidation-reduction indicator, in bacteriology as a stain, and in the dyeing industry for cotton yarns and wool.

**METHYLENE CHLORIDE** (Dichloromethane) ( $\text{CH}_2\text{Cl}_2$ ) is a colourless volatile liquid, of sp. gr. 1.336 and b.p.  $40^\circ\text{C}$ ., soluble in alcohol and 22\*

ether, used as a local anæsthetic, and prepared by the chlorination of methyl chloride, followed by distillation. It is used as an extraction solvent, and in specific gravity separations.

**METHYLPHENOBARBITONE (Phemitone, "Prominal")** ( $C_{13}H_{14}O_3N_2$ ) — A white, odourless, tasteless compound, namely, *N*-methyl-5-phenyl-5-ethylbarbituric acid, obtained by condensing the diethyl ester of phenylethylmalonic acid with methylurea; almost insoluble in water; soluble in alcohol, ether, chloroform, and solutions of alkali hydroxides; m.p.  $178^\circ$  to  $181^\circ$  C. Methylphenobarbitone is used in medicine as an anticonvulsant for the treatment of epilepsy.

**METHYLSULPHONAL ("Trional")** ( $CH_3(C_2H_5)C(SO_2C_2H_5)_2$ ) — A white, crystalline compound, namely, diethylsulphonemethylethylmethane; sparingly soluble in water, soluble in alcohol and ether; m.p.  $76^\circ$  to  $78^\circ$  C. It was formerly used in medicine as an hypnotic and sedative.

**METHYLTESTOSTERONE ("Neo-Hombreol M," "Perandren")** ( $C_{20}H_{30}O_2$ ) — A white, or slightly off-white, odourless, tasteless, crystalline powder, namely, 17-methyl- $\Delta^4$ -androstene-17-ol-3-one, prepared from dehydroisandrosterone by reaction with methyl magnesium iodide and subsequent oxidation; insoluble in water; soluble in acetone, alcohol and fixed oils; m.p.  $162^\circ$  to  $167^\circ$  C. Methyltestosterone possesses the physiological action of the male hormone, testosterone, and has the therapeutic advantage that it is active when administered by mouth. It is absorbed by the buccal mucosa and is usually given sublingually. For an account of its clinical uses, see F. A. Davidson, *Synopsis of Materia Medica, Toxicology and Pharmacology*, London (1944); and for a synthesis and bibliography, Schwenk, *The Chemistry and Physiology of Hormones* (Amer. Ass. Adv. Sci., 1944). (See Testosterone Propionate.)

**METHYLTHIOURACIL** ( $C_5H_6ON_2S$ ) — A white or slightly off-white, odourless powder, namely, 2-mercapto-4-hydroxy-6-methylpyrimidine,  $HS.C:N.C(CH_3).CH.C(OH):N$ , prepared by condensing together  
 [thiourea and acetoacetic ester; sparingly soluble in water; slightly soluble in alcohol; soluble in solutions of alkali hydroxides. Methylthiouracil has the property of reducing the activity of the thyroid gland and is used in medicine for the treatment of hyperthyroidism. It is considered to be less toxic than thiouracil. (See Thiourea, and Thiouracil.)

**"METOL"** — A trade name for monomethyl-para-aminophenol hydrochloride, or monomethyl-para-aminophenol sulphate, used as photographic developers. As prepared in several ways they are quite innocuous, but unless carefully purified, very irritating to the skin and raise blisters. The sulphate preparation can be prepared by heating quinol with aqueous methylamine under pressure, and pouring into sulphuric acid; it is somewhat soluble in water.

**"METRAZOL"** — See Leptazol.

**METRE** — See Weights and Measures.

**METRIC SYSTEM** — See Weights and Measures.

**MEV** — Million electron volts. (See Nuclear Chemistry.)

**MEXICAN POPPY OIL** — See Argemone Oil.

**MG.** — One-thousandth part of a gram.

**MICA** — The somewhat general name of a number of lustrous, laminated, hard, silicate minerals of *micaceous* character, including *muscovite*, or common mica ( $3\text{Al}_2\text{O}_3 \cdot \text{K}_2\text{O} \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ), of crystal system No. 5, and sp. gr. 2.7 to 3.0; hardness about 2; characterized by their cleavage in one direction. For the most part they are hydrous silicates of aluminium of varying and complicated composition, some being associated with potassium, lithium, magnesium, iron, etc. The chief supplies come from India, Canada, Sweden, and the United States, but there is a growing industry in Brazil, Madagascar, and the Argentine. Muscovite is readily hydrolysed by heating with water, and gradually approaches kaolinite in composition. The preparation of artificial mica has been announced.

Mica finds use as a substitute for glass in windows of lanterns, and the front of stoves, being non-flammable and not liable to fracture with changes of temperature. It would appear to have some value as a fertilizer in soils deficient in potash content. The variety known as *muscovite* is a potash mica and occurs at places in New Hampshire and China in large sheets of a yard or more in width, and it also occurs abundantly in Sweden and Norway. Its high electrical resistance and other properties have led to very extensive applications in the electrical industries. (See "Electrical Properties of Micas" (*Journal of the Franklin Institute*, September, 1931); Biotite, Lepidolite, and Phlogopite.)

**MICA BOARD** or "**MICANITE**" — the subject of an important industry in the United States — is prepared from scrap mica, the cement used being shellac. India possesses a monopoly in production of shellac, and mica abounds in that country.

**MICELLES** — See Cellulose, and Colloid Chemistry.

**MICRO** — Prefix signifying "a millionth part of" in the metric system.

**MICROBES** or **MICRO-ORGANISMS** — See Bacteria.

**MICROCHEMISTRY**, as originated and developed by Pregl, deals with minute amounts of substances and finds applications in various reactions and analyses, in the identification of some crystalline bodies, colloid chemistry, and biochemical work. It involves the use of delicate balances, the average amount of material required being about 4 milligrams. (See *Micro-Chemical Laboratory Manual*, by F. Emich (Chapman and Hall, London); *Practical Chemistry by Micro-Methods*, by E. C. Gray (Heffer and Sons, Cambridge); and Macrochemistry.)

Since 1937, *Ind. Eng. Chem., Anal. Edit.*, which was changed to *Anal. Chem.* in 1947, publishes a section devoted to Microchemistry.

**MICROCOMBUSTION** — See Combustion.

**MICROCOSMIC SALT** (Sodium Ammonium Phosphate) — See Sodium (Phosphates).

**MICROMETER** — Instrument used in conjunction with a microscope to measure small distances, diameters, and angles.

**MICRON** — A linear measure equal to  $\frac{1}{1000}$  part of a millimetre—the limit of microscopic visibility. Smaller particles are known as sub-microns.

**MICROPLASTOMETER** — Instrument to study that part of the plastic flow curve of oils, paints, and varnishes that is due to "slippage," and for the determination of the viscosity and yield values.

**MICROSCOPY** — Microscopes are instruments so constructed as to magnify objects larger than one five-thousandth of a millimetre. When made with only one lens, the instrument is termed a simple microscope, but when fitted with two or more it is known as a compound microscope. Among the many important uses of these instruments may be mentioned their application to the examination of crystals, yeasts, paper pulps, the suitability of moulding-sand for fine castings, cotton fibres, pigments, the cohesion and segregation of metals, etc.

The ultramicroscope is one of high power, so arranged that by the aid of intense localized light, the intensity of reflection of the substance under examination is greatly increased, thus correspondingly increasing the power of vision. This is effected by dipping the object-glass of the microscope into the subject liquid as contained in its glass cell, and allowing a powerful beam of light from the sun or an arc lamp to be focused by a lens on the liquid just below the microscope. In this way, the light that is scattered from the floating particles causes them to appear as bright specks. Particles as small as 1.7 millimicrons in diameter have been measured by this means, which finds useful application in the study of colloid chemistry. (See Micron.)

*References:* *The Microscope and its Revelations*, by W. B. Carpenter (J. and A. Churchill, London); *A Handbook of Chemical Microscopy*, by E. M. Chamot and C. W. Mason (Chapman and Hall, London); *Practical Photomicrography*, by J. E. Barnard and F. V. Welch (E. Arnold and Co., London); "The Polarizing Microscope in Colloidal Chemistry," by E. R. Chrystall (*Ind. Chem.*, **8**, 144 (1932)); "Chemical Applications of the Polarizing Microscope," by N. H. Hartshorne (*Chem. and Ind.*, **52**, 367 (1933)); "Industrial Microscopy," by C. H. Butcher (*Ind. Chem.*, **9**, 296 (1933)); *Industrial Microscopy*, by W. Garner (Sir Isaac Pitman and Sons, London); *Practical Microscopy*, by Martin and Johnson (Blackie and Son, London); *Recent Advances in Microscopy (Biological Applications)*, edited by A. Piney (J. and A. Churchill, London).

**MICROTOME** — An instrument for cutting thin sections of materials for microscopical examination.

"**MILBAN**" (Du Pont) — Trade-mark for a fungicide containing zinc dimethyldithiocarbamate. Used as a preventive agent against mildew and fungi on paper and textiles.

**MILDEW** — A general name applied to certain fungi, some of which form white patches on damp articles, plants, and foods. (See Fungi.)

A dressing which is recommended to combat mildew and other fungi even in the tropics is 10 per cent. neatsfoot oil, 10 per cent. mineral oil, 10 per cent. cyclohexanone, 2 per cent. *p*-nitrophenol and the remainder either perchloroethylene (preferable because non-flammable) or Stoddard's solvent. (See "Milban.")

**MILK** — The sole natural food of all the mammalia for some time after birth. There are variations in the quantities and composition of cows' milk due to differences in breed, age, feeding, and other factors. English cows give from 700 to 1,000 gallons of milk during one lactation period. It contains on average 87.35 per cent. water, 3.75 per cent. fat, protein, milk-sugar, and certain salts, the relative proportions varying with the species. Cows' milk has a sp. gr. of from 1.029 to 1.034 at 15.5° C., contains about 14 per cent. of solids, of which about 4 per cent. is fat, 3.8 per cent. casein, 4.5 per cent. lactose, and gives about 0.7 per cent. of ash. The ash of normal milk has been given by Fleischman as follows :

K <sub>2</sub> O (partly as Chloride)	24.5 per cent.	Fe <sub>2</sub> O <sub>3</sub>	.. .. . 0.3 per cent.
Na <sub>2</sub> O (partly as Chloride)	11.0 ..	P <sub>2</sub> O <sub>5</sub>	.. .. . 26.5 ..
CaO .. .. .	22.5 ..	SO <sub>3</sub>	.. .. . 1.0 ..
MgO .. .. .	2.6 ..	Cl	.. .. . 15.6 ..

N.B. by Author.—Deduct oxygen equivalent to the chlorine, and the total becomes 100.5.

It is required in Britain to contain not less than 3 per cent. fats and 8.5 per cent. other solids. The freezing-point of ordinary milk lies on average about -0.54° C., and some use is made of this fact in determining its possible adulteration with water. In souring, the milk-sugar is converted into lactic acid. (See Lactic Acid.)

The so-called "condensed milk" is made by evaporating off a quantity of its water—to about one-quarter of its original bulk—sugar being generally added at the same time. It keeps well, but when made from skimmed milk it is not so nourishing as fresh milk. Its thickening upon storage in tins, stated sometimes to be due to bacterial action, really results from chemical and physical changes. (See *Condensed Milk*, by A. Miyawaki (Chapman and Hall, London).) "Evaporated milk" is milk that is canned after a portion of its water has been removed. "Dried milk" is milk that is almost completely dehydrated, and proves a great boon where fresh milk is difficult to procure. Pure dried milk is soluble when carefully prepared, and can be stored for months without loss of physiological value, and if the fat be first removed, the dry skim milk will keep indefinitely in tins, but is liable to deteriorate through growth of micro-organisms if it contains more than 6 per cent. water. As neutral refined coconut fat can also be kept for a long time without rancidity, these two materials can be emulsified into a milk, thus providing wholesome food where fresh milk is not available. Reconstituted cream is also now commercially produced by the emulsification of milk-powder, butter, and pure water.

The so-called **pasteurization** of milk is practised in order to partially

sterilize it, and thus ensure, to some extent, the destruction of disease-producing organisms. No milk can be sold as "pasteurized" unless it has been maintained at between 145° F. (63° C.) and 150° F. (65·5° C.) for not less than thirty minutes; it must not be heated more than once, and after pasteurization it must not contain at any time more than 30,000 bacteria per c.c.

Drum-dried whey is suitable as cattle food, while whey concentrated *in vacuo* at 60° C. or less and in the presence of chalk gives lactose of good quality upon crystallization. (See Lactose.)

Goat's milk (Egyptian) is stated to contain from 10·65 to 16·55 per cent. total solids (or mean 12·54 per cent.); fat from 2·45 to 7·35 per cent. (or mean 4·04 per cent.); and the butter churned from it to have a sap. v. of from 212 to 244 and i.v. of 20·7 to 29 (Hübl).

The average composition of various milks is stated as follows:

Kind				Casein	Lactalbumin	Fat	Lactose
Cow	..	..	..	3·02	0·53	3·64	4·88
Woman	..	..	..	1·03	1·26	3·78	6·21
Goat	..	..	..	3·20	1·09	4·78	4·46
Ewe	..	..	..	4·97	1·55	6·86	4·91
Mare	..	..	..	1·24	0·75	1·21	5·67
Ass	..	..	..	0·67	1·55	1·64	5·99

*References:* *Condensed Milk*, by A. Miyawaki (Chapman and Hall, London); *Dairy Chemistry*, by H. D. Richmond (C. Griffin and Co., London); *A Textbook of Dairy Chemistry*, by E. R. Ling (Chapman and Hall, London); *Byproducts from Milk*, by E. O. Whittier and B. H. Webb (Reinhold Publishing Corp., New York); and *Dairy Bacteriology*, by B. S. Hammer (Chapman and Hall, London).

**MILK SUGAR** — See Lactose.

**MILLBOARD** — A material of various thickness, prepared from paper of various qualities and used for binding and making boxes (cartons).

**MILLERITE** — Mineral nickel sulphide (NiS), of crystal system No. 3, and sp. gr. 4·5 to 5·5, occurring at Lancaster in Pennsylvania.

**MILLI** — Prefix signifying "a thousandth part of" in the metric system.

**MILLON'S TEST**, for albuminoids in suspected tissues, consists in moistening with a solution of 2 parts mercury dissolved in 4 of nitric acid of sp. gr. 1·40, and gently warming, when an intense red colour is produced if albuminoid matter be present; this colour is not destroyed by boiling with water or exposure to the air, and is due to the presence of tryptophane residues.

**MILLS** — See Grinding.

**"MILTON"** — A proprietary antiseptic solution consisting of a hypertonic solution of sodium hypochlorite. It has been used for the continuous irrigation treatment of burns. (See "Burns, a Major Problem

of War Medicine,” by G. Lapage (*Discovery*, 1945, 14); Dakin’s Solution, and “Eusol.”)

**MIMOSA BARK** — The produce of the *Acacia mimosa*, containing an astringent principle used in tanning, and resembling cutch in character and composition. (See Catechu.)

**MINERAL ACIDS** — A general name given to all acids other than those of organic character, but especially applied to hydrochloric, nitric, phosphoric, and sulphuric acids.

**MINERAL BLACK** — Carbonaceous deposits of carbonaceous shale, culm, coal, or slate prepared by grinding and levigation; for use in preparing black pigments.

**MINERAL OILS** — See Lubrication, and Petroleum.

**MINERAL RUBBER** (Gilsonite, Elaterite, Grahamite) — See Gilsonite.

**MINERAL WOOL** — See Slag Wool.

**MINERALOGY** — The study of minerals and rocks: their composition, physical characters, crystalline forms, and geological relations. (See *Dana’s Manual of Mineralogy*, by W. E. Ford (Chapman and Hall, London); *Mineralogy*, by H. A. Miers (Macmillan and Co., London and New York); *Mineralogy*, by E. H. Kraus, W. F. Hunt, and L. S. Ramsdell (McGraw-Hill Co., New York).)

**MINERALS** — Rocks and other inorganic materials found naturally. As broadly defined by Moses and Parsons a mineral is “a homogeneous substance of definite composition found ready-made in nature, and not a product of the life or decay of an organism,” and usually possesses “a definite and characteristic crystalline structure.” The properties of minerals that are considered most important are colour, lustre, streak, crystalline form, hardness, cleavage, density, index of refraction, and X-ray pattern. The output of minerals in the various countries is given in “*The Mineral Industry of the British Empire and Foreign Countries*” (Imperial Institute, His Majesty’s Stationery Office, London), including production, imports, and exports by countries; and *Minerals Yearbook* (annual), U. S. Bureau of Mines (Superintendent of Documents, Washington, D.C.), for complete data on United States production and developments, and for many data for the world. *World Mineral Atlas* is in preparation under the joint efforts of the U.S. Bureau of Mines and the University of Maryland, to include the location of major mineral deposits, potential reserves, composition and grade of ores, comparative production and consumption by countries, salient facts on geology, mining, beneficiation, uses, and substitutes. (See W. Cullen on “The Mineral Resources of the Empire” (*Journal of the Institute of Chemistry*, 1932, Part I, 37); T. Crook on “The Geochemistry of Mineral Resources” (*J. Inst. Chem.*, 1933, Pt. 2, 122); and Ores.)

**MINIUM (Red Lead)** — See Lead (Oxides).

“**MINOFOR METAL**” — An alloy of 68.5 parts tin, 18.2 antimony, 10 zinc, and 3.3 copper, harder than Britannia metal; used for making forks, spoons, coffee and tea-pots, etc.

**MIRBANE (OIL or ESSENCE OF)** — See Nitrobenzene.

**" MISCH METAL "** — A mixture of cerium and other metals obtained from monazite sands; used in making the pyrophoric alloy ferrocerium. (See Pyrophoric Alloys.)

**MISCIBILITY** — Capability of admixture to a state of perfection. For example, vinegar can be admixed with water in all proportions, and oil of turpentine is miscible with spirits of wine. "Two substances with nearly identical internal pressures form perfect solutions; substances differing moderately show deviations roughly corresponding to the internal pressure difference; substances far apart in the series are commonly incompletely miscible." Miscibility is a property of gases also; oxygen gas can be mixed with hydrogen, for example, but solid bodies are not miscible in the same chemical sense.

**MISCOMETER** — An apparatus for obtaining a composite sample of any two (or more) miscible liquids.

**MISPICKEL** — Arsenical pyrites ( $\text{FeS}_2 + \text{FeAs}_2$ ); crystal system No. 4, and sp. gr. 5.7 to 6.3. (See Arsenic.)

**" MITIGAL "** — See Mesulphen.

**MIXING** — Mixing is used to bring two or more substances into intimate contact in order to promote some physical or chemical reaction between them. A mixture may be a powder, paste, slurry, emulsion, solution, foam, or mist according to the physical state and miscibility of the components.

The mixing of liquids with each other, or with solids or with gases, is often carried out in a cylindrical vessel provided with a stirrer. The vessel may be jacketed or furnished with heated or cooling coils. In this class are single and double-paddle mixers, propeller mixers, and turbo-mixers (a propeller moves the liquid axially, a turbo-rotor flings it out radially). If a gas is to be mixed, it is bubbled into the liquid at a point where the turbulence is high. Where a single revolving stirrer is used it tends to set the liquid charge rotating as a whole. Fixed baffles in the vessel prevent this and secure better mixing.

Power input per unit volume of liquid is often taken as a measure of the degree of agitation in a particular type of apparatus. This is only so in the range where viscosity effects are negligible. For paddle mixers 0.5–0.75 horse-power per 1,000 gallons for smooth vessels is required, 4–5 per 1,000 gallons for vessels containing coils or baffles, although 6–7 per 1,000 gallons may be required for very viscous liquids in vessels containing baffles.

The design of mixers is a field in which the use of scale models of full-sized units is useful. W. Buche has described a method of designing a large-scale mixer from the performance of a laboratory model (*Z. Ver. deut. Ing.*, 81, 1065 (1937)), and Perry's *Chemical Engineers' Handbook* discusses the same topic. Hixson and co-workers have published a number of papers correlating the performance of scale model mixers.

Another method of mixing two liquids is by passing them together

through a centrifugal pump followed by a sufficient length of pipe. Pump mixing is not very efficient, but it is sometimes convenient if the liquids have to be pumped. Immiscible liquids or liquids and powdered solids may be very intimately mixed in a Colloid Mill (see same).

A liquid may be mixed with a gas and at the same time raised to a higher level by means of the Air Lift (see same). In the Feld Gas Washer, rotating discs throw a succession of liquid sprays across a stream of gas travelling upwards through the washer. The ordinary Packed Tower (see same) is a means of mixing either liquids and gases or immiscible liquids in countercurrent flow.

Powdered solids may be mixed by tumbling them in a revolving drum. Some grinding mills also act as mixers, *e.g.*, the edge runner mill, tube mill, and ball mill.

*References*: Standard works listed under Chemical Engineering; A. W. Hixson and S. J. Baum, *Ind. Eng. Chem.*, **33**, 478 (1941); **34**, 194 (1942); also earlier papers by Hixson and co-workers in *Ind. Eng. Chem.* from 1931 onwards; J. J. Martin, *Trans. Amer. Inst. Chem. Engrs.*, **42**, 777 (1946); R. B. Olney and G. J. Carlson, *Chem. Eng. Progress*, **43**, 473 (1947); Symposium on "Agitating and Mixing" in *Ind. Eng. Chem.*, **36**, 487-531 (1944); *Agitating, Stirring, and Kneading Machinery*, by H. Seymour (E. Benn, Ltd., London); and *Mechanical Mixing Machinery*, by L. Carpenter (E. Benn, Ltd., London).

**MIXTURES** — Mechanical mixtures as distinct from chemical compounds. (See Chemical Compounds, and Diffusion.)

**ML.** — One-thousandth part of a litre.

**MODERATOR** — See Nuclear Chemistry.

**MODULUS OF ELASTICITY (Young's Modulus)** — The ratio of stress to strain within the elastic range.

**MOHS' SCALE** — For determining the hardness of solids, especially minerals, the following scale—named after Frederick Mohs, German mineralogist—is in common use:

Hardness 1, by talc, feels greasy and is easily scratched by the finger-nail.

„ 2, by gypsum, just scratched by the finger-nail.

„ 3, by calcite, scratches and is scratched by a copper coin.

„ 4, by fluorite, not scratched by copper coin, and does not scratch glass.

„ 5, by apatite, just scratches glass, and is easily scratched by a pocket-knife.

„ 6, by orthoclase, just scratched by a file, and easily scratches glass.

„ 7, by quartz, not scratched by a file.

„ 8, by topaz.

„ 9, by corundum.

„ 10, by diamond.

**MOISTURE and CHEMICAL CHANGES** — See Chemical Interactions, Heat, Oxygen, and Water.

**MOL (MOLE)** — Gram-molecule or molecular weight in grams.

**MOLASSES (Treacle)** — Uncrystallizable drainings from sugar, used to make ethyl alcohol, and to some extent for making glycerol. It contains generally about 50 per cent. invert sugar, potassium and other salts, the Java molasses having a much higher invert sugar content than beet molasses, which, however, contains a higher proportion of various salts. It is used as food, also variously for sweetening purposes, the manufacture of industrial alcohol, and the manufacture of rum (by fermentation and subsequent distillation of the fermented product). A low-grade cane molasses is known as "blackstrap," and from this material industrial alcohol is quite widely manufactured by fermentation with a specially prepared yeast. The molasses has a composition as follows: invert sugar, 16 to 18 per cent.; sucrose, 36 to 38 per cent.; water, 20 to 22 per cent.; salts and carbohydrates, 22 to 28 per cent. The alcohol thus produced contains 95-63 per cent., and about  $\frac{1}{2}$  of 1 per cent. of the alcohol produced is obtained as fusel oil (used for making amyl acetate) consisting of 8 per cent. ethyl alcohol, 12 per cent. normal propyl alcohol, 42 per cent. isobutyl alcohol, and 38 per cent. isoamyl alcohol.

A certain amount of potassium carbonate is recoverable from the aqueous residue of beet-sugar molasses after fermentation and distillation of the resulting alcohol by carbonization and calcination.

Molasses residues in association with other materials have been advocated for use in making binders for anthracite coal briquettes. For feeding cattle, cane molasses is much preferable to the beet product, which contains aspartic acid and betaine and possesses an unpleasant taste and smell. (See Binkley and Wolfrom (*J. Amer. Chem. Soc.*, **70**, 290 (1948)); Glycerol, Sugar, and Vinasse.)

**MOLECULES and MOLECULAR WEIGHTS** — The molecular theory of matter assumes that substances are made up of small independent units called molecules; that a molecule may be in certain cases (see below) one atom or a group of atoms; that all of the molecules of one substance are the same; that molecules of different substances are different; that the mass of a molecule is the sum of the masses of the atoms of the elements of which it is composed; that a molecule is "the fundamental unit" of a substance possessing the properties by which the substance is known. It should be noted that the term molecule may refer to either an element or a compound. It is correct to speak of a molecule of oxygen or a molecule of water. On the other hand, the term atom refers only to elements and not to compounds (see Atoms). While it is evident that molecules of a compound must consist of at least two different atoms, for example, water contains two atoms of the element hydrogen and one atom of the element oxygen, yet we may wonder if an elementary substance, such as nitrogen gas, consists of individual atoms or whether two or more

of the nitrogen atoms have united to form "the fundamental unit" by which we recognize the element nitrogen, that is, the nitrogen molecule. Experiment has shown that in some cases the molecules of some elements are composed of single atoms, others have two atoms to a molecule, and others have three or more atoms to a molecule. For example, helium, neon, and the other rare gases contain one, and only one, atom per molecule. On the other hand, gases like oxygen, hydrogen, nitrogen, and chlorine contain two atoms per molecule, and ozone (an allotropic form of oxygen) contains three atoms per molecule. Elements in the solid state may contain several atoms in "the fundamental unit," since in the case of sulphur there is evidence that there are eight atoms of sulphur in the fundamental rhombic unit.

In the light of the above discussion it is apparent that a molecule is in a sense the smallest imaginable particle of a given substance that is capable of a separate existence. It should be pointed out that the complexity of a molecule depends upon not only the complexity of the compound but also upon the existing conditions of the molecule; for example, the molecule of solid sulphur in the rhombic form contains eight atoms of sulphur ( $S_8$ ), while the molecule of gaseous sulphur contains four ( $S_4$ ) or two ( $S_2$ ) atoms, depending upon the temperature.

In some compounds (electrovalent or polar compounds, mostly solids, whose melt or solutions conduct the electric current) it is difficult to talk about a molecule because "the fundamental units" of structure are electrically charged particles called ions. For example, sodium chloride crystals are made up of a systematic checkerboard in space pattern or lattice consisting of alternate  $Na^+$  ions and  $Cl^-$  ions where literally billions of ions are involved in the formation of the smallest crystal. For these compounds the formula (see Symbols, Formulas), *i.e.*,  $NaCl$ , does not imply a molecule of sodium chloride, but merely that  $NaCl$  represents the ratio in which the  $Na^+$  and  $Cl^-$  ions are present.

In covalent compounds, usually electrical non-conductors, the molecules have a more realistic meaning because "the fundamental unit" is made up of a fixed number of atoms acting as a single entity. In water, two hydrogen atoms and one oxygen atom make up a single entity known as the water molecule having the formula  $H_2O$ .

The **molecular weight** of a substance is an item of importance to the chemist. Just as the individual atoms of the various elements can be assigned weight numbers which express their weights in relation to a standard ( $O=16.000$ ), so molecules whether single atoms, or clusters of atoms, have weights relative to oxygen. These weight numbers, called molecular weights, are the sums of the atomic weights of the atoms making up the molecule. Thus, the molecular weight of water ( $H_2O$ ) is  $(2 \times 1.008) + 16.000 = 18.016$ . The molecular weight of a substance expressed in grams is called its *gram-molecular weight* or mole weight for short. The gram-molecular weight of water would be 18.016 grams of water.

The gram-molecular weight of all substances contains the same number of molecules and is therefore a very convenient quantity with

which to work. For example, the gram-molecular weights of water (18.016 grams) and of chlorine (70.914 grams) contain the same number ( $6.023 \times 10^{23}$ ) of individual molecules of water and chlorine. The volume occupied by a gram-molecular weight of a substance is its *gram-molecular volume*. For liquids and solids this volume depends upon the density of the material, but for all gases this volume is constant if measured at standard temperature ( $0^\circ \text{C.}$ ) and pressure (760 mm. of Hg.) and has the value 22.414 litres. For example, 32.000 grams of oxygen, 2.016 grams of hydrogen, and 4.003 grams of helium will each occupy 22.414 litres at standard temperature and pressure (S.T.P.) and each will contain  $6.023 \times 10^{23}$  molecules of their respective gases.

Use is made of the gram-molecular volume concept to determine the molecular weight of substances that are gaseous or that can be converted into the gaseous state (vapours). In its simplest application all that is required is to weigh 22.414 litres of the gaseous material at standard temperature and pressure and obtain directly the molecular weight (Avogadro-Cannizzaro principle). Practically, however, a volume less than 22.4 litres and conditions other than standard temperature and pressure are more convenient to use. When this is done the experimental data must be converted to 22.4 litres and standard conditions by utilizing the gas laws (see Gas Laws).

The molecular weight of a non-volatile, covalent substance, for example, urea, alcohol, or sugar, which dissolves in water or some other solvent as single molecules (not ions or aggregates of molecules), can be determined by measuring the effect of a given concentration in lowering the vapour pressure, or in decreasing the freezing point, or in raising the boiling point of the solvent. It has been determined that a one molal (see Concentrations) water solution of any non-volatile solute, like sugar, lowers the freezing point of water  $1.86^\circ \text{C.}$ , or elevates the boiling point of water by  $0.518^\circ \text{C.}$  Each solvent has its own characteristic molal constant for freezing point and boiling point (see Table opposite). If the change in freezing or boiling point caused by a known amount of non-volatile, covalent solute in a given amount of water is determined, it is relatively easy to calculate the weight of solute that when dissolved in 1,000 grams of solvent would cause a change of  $1.86^\circ \text{C.}$  in the freezing point, or  $0.518^\circ \text{C.}$  in the boiling point. For example: The freezing point of water was determined to be  $0.000^\circ \text{C.}$  on a given thermometer. A solution, containing 0.775 grams of ethylene glycol dissolved in 50.0 grams of water, froze at  $-0.468^\circ \text{C.}$  Since molal concentration is the number of molecular weights of solute in 1,000 grams of water there will be  $\frac{0.775}{50.0} = \frac{X}{1,000}$ , and  $X = 15.5$  grams of solute per 1,000 grams of water. The depression of the freezing point is proportional to the molal concentration, that is  $\frac{0.468}{1.86} = 0.25$  molal. Therefore, 15.5 grams is 0.25, that is, one-fourth of a molecular weight, and so  $15.5 \times 4 = 62.0$  grams is the molecular weight.

The molecular weights determined by the above-mentioned methods (gases, liquids, and solids) are likely to be only approximate, due to

theoretical and experimental errors. If, however, this information is used in conjunction with a very accurate chemical analysis wherein the combining ratio and simplest formula have been determined, then the exact molecular weight can be ascertained. The molecular weight will be either equal to or some whole-number multiple of the simplest formula weight. The approximate molecular weight, experimentally determined, will then indicate the magnitude of this whole-number multiplier. For example, chemical analysis indicates the simplest formula of ethylene glycol to be  $\text{CH}_3\text{O}$ . Using atomic weights the formula weight will be  $(1 \times 12.010) + (3 \times 1.008) + 16.000 = 31.034$ . The exact molecular weight must be equal to this number or some whole-number multiple of it. The experimental molecular weight from freezing-point data indicates a weight of about 62. Since 62 is about  $2 \times 31.034$  evidently the exact molecular weight is  $2 \times 31.034 = 62.068$ .

MOLAL BOILING-POINT AND FREEZING-POINT CONSTANTS OF  
TYPICAL SOLVENTS

Solvent	Boiling Point Constant, ° C	Boiling Point, ° C.	Freezing Point Constant, ° C.	Freezing Point, ° C.
Acetic acid .. ..	3.07	118.1	3.90	16.7
Acetone .. ..	1.71	56.0	—	—
Benzene .. ..	2.53	80.1	5.12	5.5
Carbon tetrachloride ..	4.80	76.8	—	—
Chloroform .. ..	3.63	60.2	—	—
Ethyl alcohol .. ..	1.22	78.5	—	—
Heptachloropropane ..	—	—	12.0	29.5
Methyl alcohol .. ..	0.88	64.7	—	—
Naphthalene .. ..	5.65	218.0	6.9	80.2
Phenol .. ..	3.56	181.4	7.27	42.0
Water .. ..	0.518	100.0	1.86	0.0

The molecular (particle) weight of colloidal particles can be determined by means of the ultra-centrifuge.

*References:* *Structure of Molecules and the Chemical Bond*, by Y. K. Syrkin and M. E. Dyatkina (Interscience Publishers, New York); *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, by Linus Pauling (Cornell University Press); *Modern Chemistry*, by A. J. Berry (Cambridge Univ. Press); *Valency. Classical and Modern*, by W. G. Palmer (Cambridge Univ. Press).

**MOLYBDATES** — Compounds formed by the action of bases (such as the alkalis) on molybdenum trioxide; sodium dimolybdate is  $\text{Na}_2\text{Mo}_2\text{O}_7$ .

**MOLYBDENITE** ( $\text{MoS}_2$ ); crystal system No. 3, hardness about 1.5, sp. gr. about 4.7, and resembling graphite in appearance.

**MOLYBDENUM (Mo) and its Compounds** — Atomic weight, 95.95. See Elements for other data. Molybdenum is contained in the mineral *molybdenite* ( $\text{MoS}_2$ ), which is found in Australia, the U.S.A., Bohemia, Canada, and Sweden. It also occurs in *molybdenum ochre* ( $\text{MoO}_3$ ); *wulfenite* ( $\text{PbMoO}_4$ ); and *molybdite* ( $\text{Fe}_2\text{O}_3 \cdot 3\text{MoO}_3 \cdot 7\frac{1}{2}\text{H}_2\text{O}$ ), which often accompanies molybdenite.

Upon roasting the native sulphide in a current of air, the sulphur is burnt off as sulphur dioxide, molybdenum trioxide being left behind, and by mixing this with oil and charcoal and then strongly heating the mixture, the molybdenum is reduced to the metallic state. The metal is also prepared by alumino-thermic reduction of molybdic acid ( $\text{H}_2\text{MoO}_4$ ) (a white powder slightly soluble in water), which can be readily prepared from the trioxide.

As prepared from low-grade ore for the direct addition to steel, calcium molybdate is of growing importance, and progress has been made in the electrolytic production of molybdenum from fused bauxite admixed with calcium molybdate, as also by the electrolysis of molybdenum sodium chloride. Calcium molybdate is a white, crystalline compound obtained by fusion of calcium oxide with a molybdenum ore, while normal barium, strontium, and lead molybdates can be obtained, according to V. G. Aranda, by fusion of chlorides of the metals with normal sodium molybdate.

#### MOLYBDENUM ORE AND CONCENTRATES, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country				Molybdenum Ore and Concentrates as Mo Content Metric Tons
Norway	..	..	..	400
U.S.A.	..	..	..	14,100
Mexico	..	..	..	500
				<hr/>
				14,600
Sum of above	..	..	..	15,000

WORLD PRODUCTION, approximately the above.

Molybdenum metal is silvery-white, ductile, difficult to fuse, and in wire form has a tensile strength about half that of tungsten or steel wire. There are only a few applications for the pure metal, *i.e.*, targets for X-ray radiation, and wire and sheet. It is employed chiefly as an alloying element in steels and cast irons for unusual combination of physical properties. Wide uses of molybdenum-containing steels have been made in high-speed cutting tools, in aircraft structural parts, in automotive and railroad designs, in steam and jet turbines for high-temperature services, in armament, in corrosion-resistant steel, and in

permanent magnets. (See *Molybdenum, Cerium and Related Alloy Steels*, by H. W. Gillett and E. L. Mack (Reinhold Publishing Corp., New York), and *The Alloys of Iron and Molybdenum*, by J. L. Gregg (McGraw-Hill Book Co., New York) ; *Rarer Metals*, by Jack De Ment and H. C. Duke (Chemical Publishing Co., Brooklyn).)

**Oxides** — When heated in the air to 600° C. molybdenum oxidizes into a yellow trioxide ( $\text{MoO}_3$ ) powder (familiarily known as molybdic acid). Other oxides are the dioxide ( $\text{MoO}_2$ ), and the sesquioxide ( $\text{Mo}_2\text{O}_3$ ).

Four **chlorides** of molybdenum are known, namely,  $\text{MoCl}_5$ ,  $\text{MoCl}_4$ ,  $\text{MoCl}_3$ , and  $\text{MoCl}_2$ , all solids of specific gravity of 2.9 to 3.7.

**Ammonium Molybdate** ( $(\text{NH}_4)_2\text{MoO}_4$ ), prepared by the action of concentrated ammonia on the trioxide, is a white crystalline substance, soluble in acids, used in analytical work and in the manufacture of pigments.

**Ferromolybdenum** is produced directly from the sulphide in an electric furnace, or by the thermite process from the calcined ore.

**MONACETIN** — See Acetin.

**MONARDA OILS** — Three varieties of Monarda Oil have been described.

The essential oil distilled from *Monarda punctata* (American horsemint) is yellowish-red and contains from 65 to 70 per cent. of thymol, together with carvacrol, and thymohydroquinone. The oil from *Monarda fistulosa* contains principally carvacrol with only traces of thymol. A third oil has been distilled from *Monarda didyma* resembling lavender in odour.

**"MONAX"** — See Glass ("Monax").

**MONAZITE SAND** — A natural, crystalline phosphate of cerium and lanthanum, generally containing praseodymium, neodymium, and thorium compounds also, occurring in extensive sand deposits in West Borneo, Colorado, a certain part of Orissa (India), Carolina, the coast of Brazil, Tasmania, and Travancore.

The sand is freed from much of the associated lighter materials by sluicing with water and electromagnetic separation so that the purified product consists of from 85 to 90 per cent. real monazite, containing about 9 per cent. thorium oxide and 60 per cent. of cerium oxides. These in turn are subsequently converted into nitrates, in which form they are used in the incandescent mantle trade. The West Borneo variety has a thorium content of over 9 per cent. ; Brazilian monazite contains about 6 per cent. thorium oxide, the Travancore and Ceylon deposits about 9 per cent., and while some are reported to contain as much as 18 per cent., other varieties are devoid of it. The total rare earths *minus* thorium, as obtained by the electrolysis of their mixed chlorides, in alloyed form with iron, constitutes the sparking metal familiar as pipe-lighters. The thorium monazite sands are a potential source of helium, yielding about 1 litre from 1 kilogram of the sand by heating. (See S. B. Roy, in *Chem. and Ind.*, 52, 745 (1933) ; Gas Mantles, Helium, Incandescence, "Misch Metal", and Thorium.)

**"MOND" GAS** — As originally made for generating combustible gas, its production was based upon the passage of air in regulated amount through a mass of red-hot coal contained in a so-called gas producer, thus yielding a gas containing about a third of its volume of carbon monoxide, the nitrogen from the air used, and some carbon dioxide. In recent modifications of the process using air and steam (producer-water gas) some of the nitrogen of the fuel used is recovered as ammonia. (See Producer Gas, and Water Gas.)

**"MONEL METAL"** — A registered trade mark applied to an alloy obtained from an ore containing nickel and copper in the required proportions, and refined without separation of these metals. The ore occurs in the Sudbury region of Ontario. The composition of the "metal" (alloy) is approximately 67 per cent. nickel, 30 per cent. copper, 1.25 per cent. iron, 1.25 per cent. manganese, plus carbon and silicon. The specific gravity is 8.82, and the melting-point  $1,350^{\circ}\text{C}$ . It resists the action of sea-water, steam, dilute acids, and alkaline solutions; is of low heat conductivity, great tensile strength (see Metals (Ultimate Strength)), is machined readily, and is used for making superheated steam fittings and parts of chemical plant used respectively under caustic alkaline conditions and for varnish making. "Monel Metal" is commonly used in connection with utensils and furnishings related to the food industries.

**MONKSHOOD** — See Aconitine.

**MONO (MON)** — Prefix meaning one—such as one content of a substance. Examples: monobasic acid, monoacid base, monovalent radical, monohydroxy-compounds, and monoamino-compounds.

**MONOBASIC** — See Acids and Bases, and Valencies.

**MONOBUTYL ETHER OF DIETHYLENE GLYCOL** ( $\text{CH}_2\text{OH}.\text{CH}_2\text{OCH}_2.\text{CH}_2\text{OC}_4\text{H}_9$ ) — A high-boiling organic solvent, d. 0.957, b.p.  $232.1^{\circ}\text{C}$ .,  $n_D$  1.4258, flash point  $230^{\circ}\text{F}$ ., miscible with water. Synonym: "Butyl Carbitol."

**MONOBUTYL ETHER OF ETHYLENE GLYCOL** ( $\text{CH}_2\text{OH}.\text{CH}_2\text{OC}_4\text{H}_9$ ) — A high-boiling organic solvent, d. 0.902, b.p.  $170.7^{\circ}\text{C}$ ., miscible with water. Synonym: "Butyl Cellosolve."

**MONOCHLORBENZENE** — See Chlorobenzenes.

**MONOCHLOROACETIC ACID** ( $\text{CH}_2\text{Cl}.\text{COOH}$ ) — A colourless, deliquescent, crystalline substance of caustic character, sp. gr. 1.37, m.p.  $61.2^{\circ}\text{C}$ ., and b.p.  $189^{\circ}\text{C}$ ., prepared by action of chlorine upon hot acetic acid in presence of acetic anhydride and phosphorus (or sulphur). It is soluble in water, alcohol, and ether, and is used as an important synthetic reagent; industrially in the sodamide method of manufacturing synthetic indigo, and finds use as a corn and wart remover.

**MONOETHYLANILINE** ( $\text{C}_2\text{H}_5.\text{NH}.\text{C}_6\text{H}_5$ ) — A colourless liquid intermediate, soluble in alcohol; sp. gr. 0.963 and b.p.  $205^{\circ}\text{C}$ .; used in preparing centralite  $\text{CO}(\text{N}(\text{C}_2\text{H}_5)_2.\text{C}_6\text{H}_5)_2$ , a stabilizer in high explosives.

**MONOETHYL ETHER OF DIETHYLENE GLYCOL** ( $\text{CH}_2\text{OH}.\text{CH}_2\text{OCH}_2.\text{CH}_2\text{OC}_2\text{H}_5$ ) — A high-boiling organic solvent, d. 1.023, b.p.  $196.0^\circ\text{C}$ .,  $n_D$  1.424, flash-point  $210^\circ\text{F}$ ., miscible with water. Synonym: "Carbitol."

**MONOETHYL ETHER OF ETHYLENE GLYCOL** ( $\text{CH}_2\text{OH}.\text{CH}_2\text{OC}_2\text{H}_5$ ) — A high-boiling organic solvent, d. 0.931, b.p.  $135.1^\circ\text{C}$ ., flash-point  $111^\circ\text{F}$ ., miscible with water. Synonym: "Cellosolve."

**MONOMETHYL ETHER OF DIETHYLENE GLYCOL** ( $\text{CH}_2\text{OH}.\text{CH}_2\text{OCH}_2.\text{CH}_2\text{OCH}_3$ ) — A high-boiling organic solvent, d. 1.035, b.p.  $193.2^\circ\text{C}$ ., flash-point  $200^\circ\text{F}$ ., miscible with water. Synonym: "Methyl Carbitol."

**MONOMETHYL ETHER OF ETHYLENE GLYCOL** ( $\text{CH}_2\text{OH}.\text{CH}_2\text{OCH}_3$ ) — A high-boiling organic solvent, d. 0.966, b.p.  $124.3^\circ\text{C}$ ., flash-point  $105^\circ\text{F}$ ., miscible with water. Synonym: "Methyl Cellosolve."

**MONOVALENT (Univalent)** — See Valencies.

**MONOPHENYL ETHER OF ETHYLENE GLYCOL** ( $\text{CH}_2\text{OH}.\text{CH}_2\text{OC}_6\text{H}_5$ ) — Bacteriostatic agent, known as "Phenoxytol" (see same).

**MONTAN or MONTANA WAX** — See Lignite, and Waxes.

"**MOOGROL**" — A preparation of ethyl esters of the total fatty acids of hydnocarpus oil, used for treatment of leprosy. (See Chaulmoogra Oil, and Hydnocarpus Oil.)

**MOONSTONE** — Transparent felspar or orthoclase.

"**MORANYL**" — See Suramin.

**MORDANTS** — Chemical substances used for fixing colours in dyeing and calico-printing. (See Dyes, and Lakes.)

**MORIN** ( $\text{C}_{15}\text{H}_{10}\text{O}_7$ ) — One of the colouring matters of *Morus Tinctoria* (old fustic) related to the flavones, and synthesized by Robinson and Venkataraman. (See Fustic Extract.)

**MORPHINE** ( $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}.\text{H}_2\text{O}$ ) — An alkaloid obtained from opium, in which it occurs to the extent of from 8 to 20 per cent. It occurs as a white, crystalline solid; only sparingly soluble in water, more soluble in alcohol, slightly soluble in chloroform and insoluble in ether; it loses water of crystallization at  $100^\circ\text{C}$ . and the anhydrous form melts with decomposition at  $230^\circ\text{C}$ . It is used in medicine in the form of its hydrochloride, sulphate, or tartrate as an hypnotic, sedative, and analgesic. Morphine is considered, structurally, to be derived from phenanthrene and contains, in addition, a reduced *iso*-quinoline nucleus. For an account of the chemistry of the opium alkaloids, see Small and Lutz, Supplement No. 103 to *Pub. Health Rep.*, 1932 (H.M.S.O.); T. A. Henry, *Plant Alkaloids* (J. and A. Churchill, London). (See Diamorphine, and Opium.)

**MORPHOLINE** ( $\text{NH}(\text{C}_2\text{H}_4)_2\text{O}$ ) — A colourless, mobile liquid of a penetrating ammoniacal odour, absorbs moisture and carbon dioxide from the air, boils at  $128.3^\circ\text{C}$ ., vapour pressure 13.2 mm. at  $20^\circ\text{C}$ ., sp. gr. 1.0016, flash-point  $25^\circ\text{C}$ . It is soluble in water in all proportions; is not precipitated by salts; is immiscible with strong sodium hydroxide solutions; is a solvent for a great variety of organic substances

including phenols, alkaloids, acids, sulphur compounds, dyes ; and is used in the preparation of film-forming oil-in-water emulsions, such as polishes, leather dressings, paint and lacquer emulsions, since it gradually vaporizes from the deposited film and leaves the latter with enhanced water resistance.

Morpholine is made by treating at 50° C. *sym*-dichlorodiethyl ether with anhydrous ammonia in benzene. Several derivatives are known. (See *Ind. Eng. Chem.*, **27**, 870 (1935) ; **28**, 656 (1936).)

**MORTAR** — A mixture of 1 part (volume) burnt lime slaked with water to a thin cream and 3 parts (volumes) sharp sand, the hardening and setting of which (as when used for bricklaying) depends partly upon drying and partly upon absorption of carbon dioxide from the air by the lime, thus converting it into calcium carbonate. This carbonating effect, however, does not play much part in the hardening of the mortar. If the sand be very finely ground, calcium silicate is gradually formed. It contains about 73 per cent. sand and 6 per cent. CaO. When a quick setting is required, a varying proportion of Portland or Roman cement (up to 50 per cent.) is incorporated, according to the nature of the intended application. (See Cement, and Concrete.)

**MORTARS** — See Grinding.

**"MORYL"** — See Carbachol.

**MOSAIC GOLD (Ormolu)** — A variety of brass, being an alloy of copper and zinc in equal parts. The name is also that of a pigment made of the golden-yellow-coloured stannic sulphide. (See Tin (Stannic Sulphide).)

**MOSELEY'S ATOMIC NUMBERS** — See Elements.

**MOSS AGATE** — A variety of the mineral known as *chalcedony*.

**MOTH PROOFERS** — Para-dichlorobenzene has been reported upon favourably in the U.S.A., as also some preparations made from the cinchona alkaloids ; naphthalene, kerosene, and camphor, among other substances, are commonly used. The "Eulan" preparations are referred to under that heading, and there are British products said to be superior to them. Sodium silicofluoride to which a proportion of alum is added is also used (the aluminium ions accelerating the process), the strong solution being applied by spray or short immersion.

**MOTHER-LIQUOR** — The residual liquor after the chief constituent has been removed from a solution as far as possible by deposition or crystallization. For example, codeine, being a more soluble substance than morphine, is left in the mother-liquor after the morphine has crystallized out, and bromine is recovered from the mother-liquor from the manufacture of potassium chloride.

**MOTHER OF PEARL (Nacre)** — The brilliant, silvery, hard layer of oyster and other shells, consisting of a cellular skeleton of an albuminoid material named "conchyoline," secreted by the oyster (*Avicula macroptera* and other species), containing, according to a typical analysis, 66 per cent. calcium carbonate, water 31 per cent., and organic matter 2.5 per cent. It is extensively used for inlaying articles. (See Pearls.)

**MOTOR FUELS** — Information on this subject is given under the headings of Alcohol, Benzene, Coal, Coke, Fuel, Motor Spirit, Petroleum, and "Synthol." See G. Egloff and J. C. Morrell on "Alcohol-Gasoline as Motor Fuel" (*Ind. Eng. Chem.*, **28**, 1080 (1936)); L. M. Christensen on "Alcohol-Gasoline Blends" (*Ind. Eng. Chem.*, **28**, 1089 (1936)); L. C. Lichty and E. J. Ziurys on "Engine Performance with Gasoline and Alcohol" (*Ind. Eng. Chem.*, **28**, 1094 (1936)); O. C. Bridgeman on "Utilization of Ethanol-Gasoline Blends as Motor Fuels" (*Ind. Eng. Chem.*, **28**, 1102 (1936); and *Ind. Eng. Chem.*, **28**, 1477 (1936).

Attention has been directed to the use of alcohol blended with gasoline. One of the important considerations in the matter of such a blend is the effect of water on the miscibility of the alcohol and gasoline. O. C. Bridgeman and D. Querfeld, of the U.S. Bureau of Standards, report on studies as follows: (1) 11 gasolines were blended with 10 per cent. of alcohol, whereupon water was added to the amount of 0.4 per cent. by volume of the blend. The minimum solution temperature of the lot was found to be 15.4° C. and the maximum 36.6° C.; (2) 23 gasolines were blended with 25 per cent. of alcohol, whereupon water was added to the amount of 1.5 per cent. by volume of the blend. The minimum solution temperature of the lot was 21.9° C. and the maximum 51.7° C.

**MOTOR GREASE** is prepared in a number of varieties, ordinary soap being used in many. One recipe is as follows: lubricating oil, of sp. gr. 0.900 to 0.910, 80 parts, stearic acid 15 parts, and caustic soda 2 parts; part of the oil being melted with the stearic acid and mixed with the soda in 40 per cent. solution, the remainder of the oil being subsequently incorporated. Cheaper grades are compounded with lime soap. (See Greases, and Lubricants.)

**MOTOR SPIRIT (Petrol)** — This consists of benzol or fractional distillates from crude petroleum or "cracked" petroleum products, with or without admixture with benzol, ranging in boiling-point from about 40° to 225° C. "Straight run petrol" is petrol distilled from natural crude oil. A motor spirit is also obtained by the carbonization of bituminous coals at from 600° to 1,200° C. to the extent of about 2.5 gallons per ton (in addition, of course, to the gas, coke, and other tar products). It is also reported that colza and some other vegetable oils yield a sort of petrol by the action of molten zinc chloride.

A suggested definition of motor spirit is "any hydrocarbon spirit (other than turpentine) consisting substantially of hydrocarbons boiling below 225° C." The average final boiling point of petrol No. 1 in Great Britain is about 180° C., and that of aviation spirit 140° C. Published reports of the U.S. Bureau of Mines state that boiling ranges of Premium and Regular gasoline are, respectively, at 10 per cent. distilled 124° F. and 126° F., at 50 per cent. 218° F. and 229° F., and at 90 per cent. 327° F. and 335° F., and the respective octane numbers are 86.2 and 80.2.

Crude benzol motor spirit, unlike the refined article, shows a tendency to resinify on storage, in respect of which change tri-cresol acts to

some extent as an inhibitive. The Benzol Research Committee found that phenols in suitable amount, for a time, entirely prevent resinification under storage conditions. In the refining of petroleum the so-called hypochlorite process is used, in which motor spirit is washed with a 0.2 N. solution of calcium or sodium hypochlorite containing free alkali of from 0.5 to 1.0 gram NaOH per litre, by which means the malodorous sulphur compounds are oxidized into innocuous bodies soluble in water.

The manufacture of synthetic motor fuel is referred to under "Synthol."

(See *Motor Benzole: its Production and Use*, by Hoffert and Claxton (National Benzole Association, Ltd., London); also Coal, Cracking, Gasoline, "Motyl," Oils, Petroleum, and "Synthol.")

The so-called "**knocking**" of motor fuel causes loss of power and sometimes mechanical damage. Some of the higher paraffins are bad offenders. It has been found that "knocking" or "pinking" (detonation of the explosive charge) can be stopped by adding traces (up to 1 part in 1,000) of certain organo-metallic compounds such as tetraethyl lead ( $\text{Pb}(\text{C}_2\text{H}_5)_4$ ) to the fuel oil used in internal combustion engines. The tetraethyl lead preparation is compounded with a volatile organic halogen (such as ethylene bromide) to prevent the deposition of lead on the sparking plugs, and the mixture is known as "Ethyl fluid." Tetraethyl regulations concerning the manufacture and blending of the article have been made by the U.S. Surgeon-General's Committee.

Tests made in Australia make it appear that the addition of from 15 to 20 per cent. absolute (anhydrous) alcohol to ordinary petrol makes an ideal fuel of anti-knock character, and that alcohol is twice as efficient as benzol in stopping "knocking." Iron pentacarbonyl has also found commercial employment (see "Motyl"), but it is apt to leave a deposit of iron oxide on the sparking plugs, thus causing short-circuiting. The final report of the Departmental Committee on Ethyl Petrol (H.M. Stationery Office) states that the use of this agent is unobjectionable, subject to certain regulations detailed therein.

**Knock ratings** are stated on the basis of isoöctane (2,2,4-trimethylpentane) as 100 (and normal-heptane 0). The knock rating, or more commonly the octane rating, for some other hydrocarbons has been determined to be: normal-butane 91, isobutane 99, normal-pentane 64, 2,2-dimethylpropane 83, 2-methylbutane 90, hexane 59, 2,3-dimethylbutane 95, normal-octane 0, 1-butene 80, 2-butene 83, methylcyclopentane 82, cyclohexane 77, benzene 97, and toluene 100.

The better qualities of petrol can be used as solvents, and—in common with gasoline—for producing "air gas" for illuminating purposes and its other applications.

(See "Knocking Characteristics of Hydrocarbons" in *Ind. Eng. Chem.*, **26**, 1105 (1934); "Knocking Characteristics of Aromatic Hydrocarbons," by W. G. Lovell *et al.* (*Ind. Eng. Chem.*, **26**, 475 (1934)); "Antiknock Effect of Tetraethyl Lead," by J. M. Campbell *et al.* (*Ind. Eng. Chem.*, **27**, 593 (1935)); "Synthetic Decanes as Anti-knock Fuels" is the subject of a paper by P. L. Cramer and J. M.

Campbell in *Ind. Eng. Chem.*, **29**, 234, (1937), and the Perkin Medal address by Thomas Midgley, Jr. (*Ind. Eng. Chem.*, **29**, 241 (1937)) also contains matter that is pertinent. (See Motor Fuels, and Octane Rating.)

**MOTTRAMITE** — Mineral vanadate of lead and copper containing about 17 per cent. vanadium. (See Vanadium.)

**"MOTYL"** — A German preparation of iron pentacarbonyl in benzol in concentrated form, used in preparation of liquid fuels for use in internal combustion engines. (See Metallic Carbonyls, and Motor Spirit.)

**MOULDS** — See Fungi.

**MOURA (MOWRA) OIL** — A yellow, semi-liquid fat, soluble in ether, benzene, and carbon disulphide, extracted to the extent of about 60 per cent. from the seeds of *Bassia latifolia* (India), having an odour like that of cacao beans, and used in soap-making; sp. gr. 0.894 to 0.898, m.p. 23° to 29° C., sap. v. about 190, and i.v. about 60.

**MUCIC ACID** ( $\text{COOH}(\text{CHOH})_4\text{COOH}$ ) — An optically inactive, crystalline, dibasic acid, sparingly soluble in cold water, prepared by oxidation of dulcitol, lactose, gums, mucilage, etc.; m.p., 206–214° C., with decomposition. The process for making it from larch sawdust is based on treatment with a hydrolytic agent, and then oxidation of the resulting galactose solution ( $\text{C}_6\text{H}_{12}\text{O}_6$ ) with nitric acid at 50° to 85° C. followed by evaporation and crystallization of the mucic acid. By treating galactose with the nitric fumes from the arc process of nitrogen fixation, mucic acid can be made cheaper than tartaric acid or cream of tartar.

Mucic acid is a substitute for tartaric acid and cream of tartar in cooking, and in addition to its employment as a baking powder, it finds use in the mineral-water trade, and in the dyeing and textile industries.

**MUCILAGE** — Gum prepared from certain seeds and roots which contain large quantities of a substance which swells up with water into a mucilage. Such mucilages can be prepared from gum acacia, tragacanth, linseed, and quince seed, but the term now is often applied to any kind of adhesive paste. (See Adhesives, and Gum Arabic.)

**MUCINS** — A class of glucoproteins, insoluble in water, which occur in some secretions, and yield a class of albumins and carbohydrate upon hydrolysis.

**MULLITE** — See Sillimanite.

**MUNDIC** — A Cornish term for iron pyrites.

**MUNTZ METAL** — See Alloys, and Copper.

**MUREXIDE REACTION** — Used for the detection of uric acid and other purine derivatives, such as caffeine, theobromine and theophylline, and consisting of warming a mixture of the substance and potassium chlorate with a few drops of hydrochloric acid until the mass is dry, and then moistening it with solution of ammonia, when a purple

colour is produced. Alternatively, instead of the above, the oxidation may be carried out with nitric acid, and the product treated with ammonia as described above. The constitution of the murexide so formed is uncertain.

**MURIATIC ACID** — An old name for hydrochloric acid.

**MURUMURU BUTTER** — A fat from the seeds of the fruit of *Astrocaryum murumuru* (a kind of South American palm-tree), amounting to about 40 to 42 per cent.; sp. gr. at 15° C. 0.918, m.p. 34° to 35° C., sap. v. 240 to 241.5, Reichert-Meissl value 2.8 to 3.14, and Hanus i.v. 11.2 to 11.5. It contains stearic and possibly arachidic acid, also caprylic and capric acids. The fruit yields about 40 per cent. of oil, which is used in margarine, confectionery, cosmetics, pharmaceuticals, and for soap.

**MUSCARINE** ( $C_2H_5.CH(OH).CH(CHO).N(CH_3)_3.OH$ ) — A poisonous alkaloid contained in the fungus, *Amanita muscaria*, chemically related to choline and resembling acetylcholine in its pharmacological effects. (See Acetylcholine.)

**MUSCOVITE or POTASH MICA** ( $K_2O, 3Al_2O_3, 6SiO_2, 2H_2O$ ); crystal system No. 5, and sp. gr. 2.7 to 3.0. (See Mica.)

**MUSK** — An aromatic resinous substance obtained from the preputial follicles of the musk deer, *Moschus moschiferus*, an inhabitant of Central Asia. Most of the musk of commerce is obtained from Szeckuen (Tonquin musk) or from Thibet. The odour is due to a ketone, muskone ( $C_{16}H_{30}O$ ) which has been prepared synthetically and marketed in Switzerland under the proprietary name, "Exaltone." British Patent No. 582,326 describes the preparation of musk ketones by oxidation of the fraction of the unsaponifiable matter boiling between 130° and 170° C. at 1 mm., obtained from the fat of the musk glands of the musk rat. An alkaloid having the empirical formula  $C_{16}H_{25}N$  has been isolated from musk and named muscopolypidine. (See H. Schinz *et al.*, *Helv. Chim. Acta.*, **29**, 1524 (1946)).

Several polynitro aromatic compounds possess powerful odours resembling natural musk and are known as "artificial musk." Xylene musk, namely, 1,3-dimethyl-5-*tert*-butyl-2,4,6-trinitrobenzene, is prepared by reacting *m*-xylene with *tert*-butyl chloride and subsequent nitration; m.p. 113° C. Ambretta musk, namely, 1-methyl-2-*tert*-butyl-5-methoxy-3,6-dinitrobenzene, is prepared in a similar manner from *m*-cresol. Musk ketone, namely, 1,3-dimethyl-5-*tert*-butyl-2-acetyl-4,6-dinitrobenzene is prepared from *m*-xylene by introduction of the butyl and acetyl groups and finally nitrating; m.p. 136° C. (See Parry's *Cyclopædia of Perfumery* (J. and A. Churchill, London).)

**MUSKONE (Musccone, Muskine)** — See Musk.

**MUST** — The juice of crushed grapes as expressed for wine-making (before fermentation).

**MUSTARD (Black)** — The seeds of *Brassica nigra* (Fam. Cruciferae). It contains about 30 per cent. of fixed oil which solidifies at -17° C.; sap. v. 174; sp. gr. 1.014 to 1.103; i.v. 92 to 123; ref. ind. 1.467 to

1.475 at 15.5° C. It contains also a glycoside, sinigrin, and an enzyme, myrosin, which, in the presence of water, react together to produce allyl isothiocyanate to the presence of which the pungency of black mustard as a condiment is due. Sinigrin has been obtained in the crystalline form; m.p. 79° C.

**White Mustard** is prepared from the seeds of *Sinapis alba* (Fam. Cruciferae) and contains sinalbin, myrosin and about 25 per cent. of fixed oil. In the presence of water, sinalbin reacts with myrosin to form acrinyl isothiocyanate ( $C_7H_7SCNO$ ).

**MUSTARD GAS (Yperite)** — See Gassing.

**"MUTOCHROME"** — A battery of lenses forming a camera and projector for photography of a textile pattern or design, arranged so that a coloured image of one element thereof is given by each lens, and each of these is photographed on to the same plate.

**"MYANESIN"** — A synthetic compound, namely, 2- $\beta$ -dihydroxy- $\gamma$ -(2-methylphenoxy)propane, being one of a series of glycerol ethers investigated by F. M. Berger and W. Bradley (*Lancet*, 1, 97 (1947)) and found to possess a pharmacological action resembling that of the curare alkaloids. "Myanesin" has been used as an adjunct to anaesthesia to produce muscular relaxation (see F. B. Mallinson in *Lancet*, 1, 98 (1947); and W. H. Armstrong Davison in *Brit. Med. J.*, 1, 544 (1948). (See Tubocurarine Chloride.)

**"MYCOBAN"** (Du Pont) — Trade-mark for calcium propionate and sodium propionate. Used to delay the growth of mould and the development of rope in bakery foods.

**MYCOLOGY** — See Fungi.

**MYDRIATIC** — A substance which has the property of causing dilatation of the pupil of the eye. Notable examples of mydriatics are atropine and homatropine.

**MYELINE** — A crystalline phosphatide contained in brain matter, soluble in hot alcohol. (See Brain Matter.)

**"MYOCRISIN"** — See Sodium Aurothiomalate.

**MYOTIC** — A substance which has the property of causing contraction of the pupil of the eye. A notable example is physostigmine.

**MYRCIA OIL** — See Bay Oil.

**MYRIA** — Prefix signifying "ten thousand of" in the metric system.

**MYRICA WAX** — See Waxes (Bayberry).

**MYRICIN** — See Waxes (Beeswax).

**MYRISTIC ACID** ( $C_{13}H_{27}COOH$ ) — A fatty acid predominating in the fats of members of the family Myristicaceae, and easily isolated from the fat of the nutmeg, *Myristica fragrans*. It is soluble in hot alcohol, melts at 58° C., and is a member of the open-chain series of fatty acids.

**MYRISTICIN** — See Nutmeg Oils.

**MYROBALANS (Myrabolans)** — The dried fruit (nuts) of the Chinese and Indian trees *Terminalia bellerica*, *T. chebula*, *T. citrina*, and allied species of the N.O. Combretaceæ, containing from 25 to 50 per cent. tannin, and used, like galls, in the tanning industry. The emblic myrobalan (*Phyllanthus embilica*, N.O. Euphorbiaceæ) is very liable to attack by fungi (*Penicillium*) in the presence of moisture, and consequent loss of tannin content.

They contain a large proportion of gums, and, in the form of fine powder or extract, are used for dyeing black cotton goods; also in the indigo-dyeing industry for removing surplus dye from the fabrics, and for preparing ordinary and copying inks.

**MYRRH.** — See Gums.

**MYRTLE OIL** — An essential oil obtained by distillation from the leaves of *Myrtus communis* (Fam. Myrtaceæ) which grows in Southern France, Spain, Asia Minor and other Mediterranean countries. It is light yellow or greenish yellow in colour and possesses an agreeable odour. Myrtle oil contains cineol, *d*-pinene and dipentene; soluble in alcohol and ether; sp. gr. 0.896 to 0.920 at 15° C.; opt. rot. +10° to +30°. An alcohol, myrtenol ( $C_{10}H_{16}OH$ ), has also been isolated from the oil. It is used in perfumery.

**MYRTLE or LAUREL WAX** — See Waxes.

**n** — Normal (see Chains).

**NAAL OIL** — An essential oil distilled from Naal grass, *Cymbopogon nervatus*, which grows in the Sudan and yields from 0.8 to 1.5 per cent. by weight of the dried grass. It is light yellow in colour and resembles ginger grass oil in odour. It is known in India as "Sofia" oil. It contains *l*-limonene and perillic alcohol; soluble in alcohol; sp. gr. about 0.954; ref. ind. 1.495 at 20° C.

**NABAM (Disodium ethylene-bis-dithiocarbamate)** — A fungicide.

**"NACCONOL"** — A series of proprietary "wettters" used in dyeing fibres. (See Wetting Agents.)

**NAPHAZOLINE HYDROCHLORIDE ("Privine")** ( $C_{14}H_{14}N_2$ , HCl) — A white crystalline powder, namely, 2-(1-naphthylmethyl)-2-imidazoline hydrochloride; soluble in water and in alcohol, slightly soluble in chloroform, insoluble in ether; m.p. 255° to 260° C. Used in medicine as a local vaso-constrictor for the relief of nasal congestion.

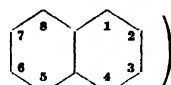
**NAPHTHA** — A more or less general term given to oily bodies produced from petroleum and by the distillation of cannel coal and bituminous shale, containing paraffin in solution of mixed hydrocarbons; used for illuminating purposes, in varnish-making, also as solvents for rubber, etc. One such liquid is found associated with deposits of bitumen and asphalt in many places, and is distilled therefrom.

Heavy Naphtha, as prepared from coal tar, is dark-coloured, has a sp. gr. of 0.925 to 0.950, and flash-point about 78.3° C. It is used as a solvent and in paint-making; also for making coumarone resins.

**Water-White Naphtha** ("Hi-flash") has a sp. gr. of 0.870 to 0.880, b.p. between 165° and 186° C., a flash-point not below 37.8° C., and is largely used as a solvent.

**Solvent Naphtha** 90/160 and 90/190 are mixtures of benzol, toluol, xylol, etc., derived from coal-tar distillation. (See Benzene, Coal, and Petroleum.)

**Wood Naphtha** (wood spirit co-called) is of alcoholic character and is marketed in the forms of "solvent" and "miscible 60 per cent." (See Alcohols.)

**NAPHTHALENE** ( $C_{10}H_8$ ; ) — A white, solid hydro-

carbon obtained from coal tar, and chiefly contained in the fraction that distils between 180° and 200° C., from which it crystallizes out on cooling, and is subsequently purified by treatment with small quantities of strong sulphuric acid, followed by sublimation.

Pure naphthalene crystallizes in white glistening plates, m.p. 80° C., b.p. 218° C., sp. gr. 1.145, and is readily soluble in hot alcohol, benzol, and ether. It has a peculiar tarry odour, and is prepared commercially in the forms of crystals, flakes, balls, powders, and sticks, and is commonly used as "moth-balls" insect repellent.

Naphthalene is largely used in the manufacture of phthalic acid, naphthylamines, naphthols, naphthalenesulphonic acids and other intermediates, "Tetralin" and "Dekalin" (by a process of hydrogenation); also for carburating illuminating coal gas. (See Lee and Kosek, Natl. Advis. Comm. Aeronautics, War-Time Report, M.R., August, 1941.)

**Naphthalenesulphonic Acids** ( $C_{10}H_7.SO_3H.H_2O$ ). Two isomers are known. The *alpha*-compound is a crystalline deliquescent intermediate, of m.p. about 85° C., soluble in water, alcohol, and ether, prepared by the interaction of naphthalene and cold sulphuric acid. When sulphonation takes place at 160° C. the *beta*-acid is produced.

There are ten naphthalenedisulphonic acids ( $C_{10}H_6.(SO_3H)_2$ ) several of which are used as intermediates. When naphthalene is sulphonated in the vapour phase much less acid is required, and there is a better production than by the use of liquid acid, the transformation into useless isomeric acids being largely prevented.

**Naphthaleneacetic Acid** — See "Parmonc."

**Mononitronaphthalene** ( $C_{10}H_7.NO_2$ ) — The *alpha*-compound, a yellow needle-like solid, of m.p. 59° C., insoluble in water, and soluble in alcohol and in carbon disulphide, is prepared by the action of mixed nitric and sulphuric acids on naphthalene, and is used in the preparation of explosives and dyes. The *beta*-compound, of m.p. 79° C., insoluble in water, and soluble in alcohol and in ether, is formed only in minute amount in the preceding nitration, and its preparation is accomplished by indirect methods.

**Dinitronaphthalene** ( $C_{10}H_6.(NO_2)_2$ ) is used in the preparation of explosives, and "alizarin black."

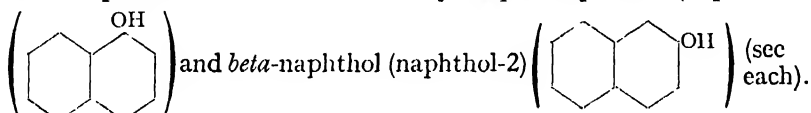
**NAPHTHENES** — Saturated cyclic hydrocarbons ( $C_nH_{2n}$ ), better known as cycloparaffins. (See Petroleum.)

**NAPHTHIONIC ACID** (*1-Naphthylamine-4-sulphonic Acid*) ( $C_{10}H_8(NH_2)SO_3H$ ) — A white crystalline intermediate, obtained by the sulphonation of *alpha*-naphthylamine, soluble in alcohol and ether, and used in the preparation of azo-dyes.

**NAPHTHOL (Alpha)** ( $C_{10}H_7OH$ ) is a colourless, crystalline substance used in making dyestuffs, which melts at  $96^\circ C.$ , and is soluble in benzol, alcohol, and ether, but only slightly soluble in water. It is prepared by fusing *alpha*-naphthalenesulphonate and caustic soda, and decomposing subsequently with hydrochloric acid and distilling.

**NAPHTHOL (Beta)** ( $C_{10}H_7OH$ ) is a white, lustrous substance of phenolic odour contained in coal tar, m.p.  $122^\circ C.$ , b.p.  $285^\circ C.$ ; soluble in benzol, alcohol, ether, and chloroform, and slightly soluble in water; made by fusing *beta*-naphthalenesulphonate with caustic soda, and subsequent distillation *in vacuo*. It is used in making dyestuffs and as an antiseptic in medicine.

**NAPHTHOLS** — Phenolic bodies derived from naphthalene by the replacement of one or more hydrogen atoms by hydroxyl groups. Two naphthols are known, namely, *alpha*-naphthol (naphthol-1)



**NAPHTHYL** — The monovalent radical  $C_{10}H_7$ .

**NAPHTHYLAMINES** used as "intermediates" include *alpha*-naphthylamine ( $C_{10}H_7.NH_2$  (1)), a colourless, crystalline compound of disagreeable odour, m.p.  $50^\circ C.$ , b.p.  $301^\circ C.$ , obtainable by reduction of *alpha*-nitronaphthalene ( $C_{10}H_7.NO_2$  (1)), and readily soluble in alcohol; and *beta*-naphthylamine ( $C_{10}H_7.NH_2$  (2)), a crystalline odourless compound, m.p.  $112^\circ C.$  and b.p.  $306^\circ C.$ , obtainable from *beta*-naphthol ( $C_{10}H_7.OH$  (2)) by action of ammonium hydroxide and sulphite. (See Naphthalene.)

**NAPLES YELLOW** — A pigment made of lead antimonate, used in the oil, paint, and ceramic industries. (See Lead (Antimonate).)

**NARCEINE** — See Opium.

**NARCOTICS** — Substances which possess the property of selectively depressing the activity of nervous tissue, producing a state of unconsciousness ranging from sleep (hypnotics) to surgical anaesthesia (anaesthetics). In concentrations high enough, most narcotics affect all the living tissues but they reduce the activity of nervous tissue in concentrations too low to influence non-nervous tissue. Various chemical substances possess narcotic properties; they include alcohol and general anaesthetics such as ether and vinyl ether, hypnotics such as barbitone and its various derivatives, and analgesics such as opium preparations, morphine, and pethidine.

In Great Britain, traffic in narcotic drugs such as morphine, opium preparations, etc., is controlled by the Dangerous Drugs Acts. These constitute part of an international agreement which was originally concluded under the Hague Convention. The corresponding legislation in the United States is the Federal Narcotic Regulations. By international agreement, the League of Nations was entrusted with the "general supervision" of the traffic in opium and other dangerous drugs. This responsibility was transferred to the United Nations Organization following World War II. (See *Poisons Law*, by H. N. Linstead (Pharmaceutical Press, London).)

**NARCOTINE** — See Opium.

**"NARKI METAL"** — A proprietary silicon cast-iron alloy containing 13 to 14 per cent. silicon, chiefly used in making plant for resisting nitric, sulphuric, and phosphoric acids. Its tensile strength is stated at one-eighth of cast iron.

**NASCENT** — A term used to indicate the state of chemical substances at the moment of their generation or liberation from combination, when they are often more active in their properties than ordinarily. It has been shown that the chemical reactivity of such gases as hydrogen, oxygen, nitrogen, and carbon monoxide is increased by bringing them in contact with solution in very minute bubbles, as obtained, for example, by forcing these gases through cartridges of paper. Hydrogen thus prepared reduces mercuric chloride to calomel, potassium nitrate to nitrite, and carbon dioxide to formaldehyde. With oxygen gas, ammonia is oxidized to nitrous acid and methyl alcohol to formaldehyde; while with nitrogen and hydrogen an indication of the production of ammonia is observed.

When hydrogen gas is passed into a solution of ferric chloride or of potassium permanganate no change results, but, if either of these solutions is acidified and zinc added, then ferric is reduced to ferrous, and permanganate to manganous. The reducing power of hydrogen evolved in electrolysis, furthermore, depends upon the metal used as cathode, for example, the potential required to liberate hydrogen gas using a lead cathode (sulphuric acid being the electrolyte) is 0.49 volt higher than with a silver cathode. Nascent state is probably very closely connected with the energy relationship of a given system. (See also Energy, Hydrogen, and Nitrogen.)

**"NATALITE"** a motor fuel made to contain either 50 per cent. or 90 per cent. by weight of alcohol and ether, and a small quantity of ammonia or trimethylamine (added to overcome the tendency of alcohol to cause corrosion). It is prepared by a fermentation process from sugar molasses in Natal. Another account gives the composition of "Natalite" as 60 per cent. alcohol and 40 per cent. ether.

**NATROLITE** — A crystalline zeolite mineral, ordinarily described of the composition  $(\text{Na}_2\text{Al}_2\text{O}_3, 3\text{SiO}_2, 2\text{H}_2\text{O})$ ; crystal system No. 4, and sp. gr. 2.24. S. di Franco (*B.C.A.*, A, 1929, 905) gives the formula  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}, 2\text{H}_2\text{O}$  to the natrolite of Viagrande (Etna). (See Zeolites.)

**NATRON (Trona)** — A crude native form of sodium sesquicarbonate found in the soda-lakes of Egypt, Hungary, Magadi, Siberia, Thibet, and elsewhere; crystal system No. 5. (See Sodium.)

**NATURAL GAS** — See Gas (Natural).

**NAULI GUM** — See Gums and Resins.

**NAVAL STORES** — See Turpentine, and Gums and Resins (Rosin).

**NEAT'S-FOOT OIL** — A pale yellow oil, of variable character and several grades, soluble in alcohol and ether, obtained in the process of boiling down ox, calves', and sheep's feet, of sp. gr. 0.914 to 0.918, sap. v. 194 to 199, i.v. 58 to 70, and ref. ind. at 20° C. 1.469; used as a leather dressing, lubricant, and for oiling wool. According to one published analysis, the sample examined contained 2 to 3 per cent. stearic acid, 17 to 18 per cent. palmitic acid, 74.5 to 76.5 per cent. oleic acid, and 5 to 10 per cent. glycerol.

**"NECOL PLASTIC WOOD"** — A material that can be moulded in the soft state and worked like ordinary wood in the dry form, capable of firm attachment to surfaces of wood, metal, or stone; useful for filling holes and making fillets on woodwork, etc. Half a pound of wet wood will cover about 1 square foot in a layer of  $\frac{1}{8}$  inch thick; 8.2 ounces of the wet wood gives 3.8 ounces of dry material. (See Plastic Wood, and "Xylolith".)

**NECTAR** — A sugary juice which collects in the nectaries or discs of flowers, containing cane sugar together with uncrystallizable sugar. The total sugar in nectar from different Australian flowers has been determined as about 6 per cent. of their weight. This nectar contains 70 to 90 per cent. water, and its concentration to a dry substance content of about 78 per cent. is effected in the sac of the bee. Other samples of nectar examined by O. W. Park contained from 40 to 55 per cent. sugar, the proportion varying considerably for any given source. (See Honey.)

**NELSONITE** — An aggregate of ilmenite and apatite containing magnetite. Locality, Virginia. A commercial source of titanium oxide paint pigment.

**"NEMBUTAL"** — See Pentobarbitone Sodium.

**NEO** — "New" or "recent." Example, neopentane, which is 2,2-dimethylpropane or tetramethylmethane ((CH<sub>3</sub>)<sub>4</sub>C).

**NEOARSPHENAMINE** — See Arsphenamine.

**"NEOCELLON"** — A patented waterproofing solution made from cellulose acetate and nitrocellulose, a suitable plasticizer (triphenyl phosphate, for example) being incorporated according to the nature of the application. A flame-proofing solution of aqueous character is also made and sold under this name, depending upon the employment of ammonium bromide and (or) ammonium phosphate, other components being incorporated to preserve the flexibility of the treated articles.

**NEODYMIUM (Nd) and its Compounds** — Atomic weight, 144.27. See Elements for other data. One of the rare-earth group of elements, belonging to the cerium group of the same. It occurs in *cerite*, *monazite sand*, etc., and has been isolated by the electrolysis of its fused anhydrous chloride. It is silver-white in appearance, tarnishes in the air, and is attacked by hot water and dilute acids.

Neodymium forms **salts** that are crystalline and generally of a rosy colour, namely, the chloride ( $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ ), the sulphate ( $\text{Nd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ), the bromide ( $\text{NdBr}_3$ ) (green colour), the bromate ( $\text{Nd}_2(\text{BrO}_3)_6 \cdot 18\text{H}_2\text{O}$ ), and the iodide ( $\text{NdI}_3$ ) (black colour). An **oxide** ( $\text{Nd}_2\text{O}_3$ ) of a pale blue colour is known, and the **hydroxide** ( $\text{Nd}(\text{OH})_3$ ) is obtained by adding alkali to a solution of its salts.

“**NEO-HALARSINE**” — See Arsphenoxide.

“**NEO-HOMBREOL M**” — See Methyltestosterone.

**NEOMYCIN** — A basic substance, being an antibiotic produced by *Streptomyces fradiae* when grown in a culture medium containing a source of nitrogen, a carbohydrate and salt under either surface or submerged culture conditions. It is soluble in water and insoluble in organic solvents, but can be easily removed from the culture fluid by the methods of adsorption and elution applicable to streptomycin. It possesses an activity against both Gram-positive and Gram-negative organisms, including organisms resistant to streptomycin and mycobacteria. It is non-toxic to animals. (See S. A. Waksman and H. A. Lechevalier, *Science*, **109**, 305 (1949).)

**NEON (Ne)** — Atomic weight, 20.183. See Elements for other data. Neon is a member of the argon group, more volatile than argon, and recognized early in the study of isotopes as consisting of atoms of mass 20 and mass 22. It exhibits no chemical characteristics. Neon is present in the air to the estimated extent of only 1 part in about 80,000; exhibits a characteristic spectrum, and has been liquefied. Vacuum tubes charged with the gas and electrically incited produce a brilliant red light. The light has a considerable penetrative power, and is used to some extent in landing lights, harbour lights for navigation purposes, and picturesque advertisement.

**NEOPRENE** (Du Pont) — Generic name for synthetic rubber made by the polymerization of 2-chloro-1,3-butadiene ( $\text{CH}_2 : \text{CCl}-\text{CH} : \text{CH}_2$ ), which is made by the reaction of vinylacetylene and hydrogen chloride. Neoprene rubber is outstanding in its resistance to oils, light, heat, and many chemicals. Used for quick setting, high strength adhesives.

**NEOSTIGMINE BROMIDE** (“**Prostigmine**”) ( $\text{C}_{12}\text{H}_{19}\text{O}_2\text{N}_2\text{Br}$ ) — A white, odourless, crystalline powder, being the dimethylcarbamic ester of 3-hydroxyphenyltrimethylammonium bromide; soluble in water and alcohol. It possesses a pharmacological action similar to that of the naturally occurring alkaloid, physostigmine, but has the advantage of greater stability. It is used in medicine, by oral administration, for the treatment of certain forms of muscular paralysis such as myasthenia gravis.

**NEOSTIGMINE METHYLSULPHATE** ("Prostigmine") ( $C_{13}H_{22}O_6N_2S$ )

— A white odourless, crystalline powder being the dimethylcarbamate ester of 3-hydroxyphenyltrimethylammonium methylsulphate; soluble in water; slightly soluble in alcohol; m.p.  $142^\circ$  to  $145^\circ$  C. It is used in medicine for the treatment of myasthenia gravis and is administered by injection.

**"NEOTHYL"** ("Metopryl") — A mobile, inflammable liquid, namely, methyl-*n*-propyl ether; sp. gr. 0.726 at  $16^\circ$  C.; b.p.  $39^\circ$  C.; soluble in 20 parts by volume of water at  $25^\circ$  C.; inflammability range identical with that of diethyl ether. It is used as an inhalation anaesthetic and is stated to be less irritant to the respiratory tract than diethyl ether. (See C. E. Sykes, *Brit. Med. J.*, **2**, 420 (1949); and Ether.)

**"NEO-VARICANE"** — See Ethanolamine Oleate.

**NEPHELINE (ELAETITE)** — A mineral of the approximate composition  $(3(Na_2,K_2)O, 4Al_2O_3, 9SiO_2)$ , found in large deposits in the Murman Peninsula (Russia), which is likely to find useful application in glass-making, as a fertilizer, and in the ceramic industries.

**NEPHELOMETRY** — A kind of photometric chemical analysis dealing with the character and size of particles in suspension and depending upon the comparison of scattered light from such precipitates. The methods of nephelometry were used by T. W. Richards in several of his researches on atomic weights of the elements. (See *Photometric Chemical Analysis*, vol. ii., "Nephelometry," by J. H. Yoe (Chapman and Hall, London); also Turbidimeters.)

**NEPHRITE (Axestone or Beilstein)** — See Jade.

**NEPTUNIUM (Np)** — Element number 93, atomic weight 237, discovered by E. M. McMillan and P. H. Abelson, in 1940, and accepted (1949) by the International Union of Chemistry. Neptunium-239 is formed by beta particle emission from uranium-239. (See Nuclear Chemistry.)

**NERNST'S HEAT THEOREM** — As the temperature,  $T$ , approaches zero degrees absolute, the change in enthalpy ( $\Delta H$ ) and the change in free energy ( $\Delta F$ ) approach each other asymptotically—they become numerically equal—for reactions in condensed systems, *i.e.*, solids or liquids.

This pronouncement, made by Nernst in 1906, was developed by him into the third law of thermodynamics, which states that "every substance has a finite positive entropy ( $\Delta S$ —see Thermodynamics), but at the absolute zero of temperature the entropy may become zero, and does become zero in the case of a perfect crystalline substance." (See Energy.)

**NERODOL** — See Tannins.

**NEROL** ( $C_{10}H_{18}O$ ) — A terpene alcohol of rose odour, of sp. gr. 0.881 and b.p.  $226^\circ$  C.; the *cis* isomer of which geraniol is the *trans*. It occurs in rose, cyclamen, bergamot, and neroli oils. Both nerol and geraniol are formed by the reduction of citral.

**NEROLI OIL (Oil of Orange Flowers)** — An essential oil obtained by steam distillation from the fresh blossoms of *Citrus Aurantium* subsp. *amara*. It is pale yellow in colour, having a slight fluorescence and becoming brownish-red on exposure to light; it contains methyl anthranilate, nerol, *l*-linalol, linalyl acetate, geranial, and limonene; soluble in alcohol and ether; sp. gr. 0.870 to 0.885 at 15° C.; ref. ind. 1.468 to 1.477 at 20° C.; opt. rot. 0° to +8°. It is used in perfumery and as a flavouring agent. (See Linalol, and Orange Oil.)

**NEROLINE (Beta-Naphthylmethyl Ether)** ( $C_{10}H_7OCH_3$ ) — A white crystalline body (m.p. 72° C.), soluble in alcohol and ether; prepared by heating a mixture of beta-naphthol, methyl alcohol, and zinc chloride; used in perfumery, and usually sold as "Veroline." It is used as a perfume.

**NESSLER'S REAGENT** — A solution of mercuric iodide in potassium iodide made alkaline by potassium hydroxide, which turns yellowish-brown even with traces of ammonia, for which it is a delicate test.

**NEURINE** — See Choline.

**NEUTRALIZATION** — The removal of acidity or alkalinity from a solution to a neutral state by means of an alkaline or acid solution respectively, as tested by litmus-paper or other indicator. (See Chemical Compounds, Litmus, pH Value, and Volumetric Analyses.)

**NEUTRALIZATION EQUIVALENT** — See Fats (Tests).

**NEUTRINO** — A particle of "negligible rest mass" that is emitted by a nucleus in beta-ray disintegration along with the electron. The presence of the neutrino is postulated to satisfy "the conservation of angular momentum principle" and to account for the continuous distribution of energy in radioactive beta-ray disintegrations.

*References:* "Table of Isotopes," by G. T. Seaborg (*Review of Modern Physics*, 16, 1 (1944)); *Applied Nuclear Physics*, by Pollard and Davidson (John Wiley and Sons, Inc., New York and London); *Nuclear Physics*, by Feather (Cambridge University Press).

**NEUTRON** — A particle that is indifferent to the strongest electrical and magnetic forces, therefore, of electrical charge, zero; of mass practically the same as the hydrogen atom, namely, 1, and first recognized by Chadwick (1932) in studies of the impacts of alpha particles from radium upon the element beryllium. (See Atoms, Nuclear Chemistry, and Radioactivity (Artificial).)

**NIACIN** — See Vitamins.

**NIACIN AMIDE** — See Nicotinamide.

**"NICAMIDE"** — See Nikethamide.

**NICKEL (Ni) and its Compounds** — Atomic weight, 58.69. See Elements for other data. Nickel occurs in combination in a number of minerals (chiefly in combination with arsenic), including *kupfernickel* ( $Ni_2As_2$ ), *white nickel* ( $NiAs_2$ ), *nickel glance* ( $Ni_2(AsS)_2$ ), *nickel blende* ( $NiS$ ), and

*melonite* (NiTe) ; also in association with cobalt in *speiss*. Kupfer-nickel deposits are found in North and South America, Norway, Germany, France, and Hungary, and other ore deposits occur in Ontario and New Caledonia, also at Blaaubank and in the Pelandsberg (Rustenberg) district of South Africa. (See also Pimelite, Millerite, Pentlandite, and Ullmanite.)

The metal can be obtained by heating nickel oxalate out of contact with air, or by reduction of the oxide with carbon at a high temperature. It is made commercially in large quantity both from the sulphide ores and the mineral *garnierite*, a hydrated silicate of nickel and magnesium ((Ni,Mg)O,SiO<sub>2</sub>,H<sub>2</sub>O) found in New Caledonia, by roasting, in which the sulphur and arsenic constituents are for the most part burned off. The resulting mixed metallic oxides are subsequently heated to from 50° to 80° C. in a stream of "producer gas." (See Producer Gas.) By this (Mond's) process oxides other than nickel are reduced to the metallic state while nickel enters into combination with the carbon monoxide, forming nickel carbonyl (Ni(CO)<sub>4</sub>), which passes off in a vaporous state, and from it the nickel is obtained by passage of the gases through a pipe heated to about 180° C., whereby the mixture is resolved into gaseous carbon monoxide (which is used over again in fresh operations), the free metallic nickel being deposited in a lustrous mirror-like form.

#### NICKEL ORE, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

	Country			Nickel Ore as Ni Content Metric Tons	
Greece	..	..	..	1,000	
Norway	..	..	..	1,000	
				-----	2,000
U.S.S.R.	..	..	..		2,000
Canada	..	..	..		100,000
Burma	..	..	..		1,000
New Caledonia	..	..			11,000
Sum of above	..	..			116,000
WORLD PRODUCTION	..	..			118,000

Nickel carbonyl in pure form (of b.p. 43° C. and sp. gr. 1.3185) can be obtained as a colourless volatile liquid, soluble in alcohol. The nickel used in making it is best prepared by reduction at 350° C. and cooled to 50° C. in a reducing atmosphere. Its vapour is poisonous and explodes at 60° C. (See Metallic Carbonyls.)

There are also electrolytic processes for preparing nickel in the form of cathode plates from the roasted ore, after leaching with acid to remove most of the copper and otherwise. Certain defects in electrolytic nickel as ordinarily produced are overcome by the destruction of associated organic matter by means of chlorination or treatment with hydrogen peroxide.

Nickel is obtained as a black powder or as a bright, lustrous, white, ductile, malleable, and hard metal. It is used chiefly for toughening steel (a large consumption going into armaments); also in the manufacture of nickel-chromium-iron alloys of heat- and acid-resisting character and nickel-copper alloys; nickel-iron alloy for use in telegraphy; alloys for making coins used in Germany, Belgium, France, and the U.S.A.; for plating iron and steel articles (as it does not readily tarnish in the air), and as a substitute for tin in such coatings. While nickel is corroded to some extent in cooking operations—less than tin or aluminium—the preparation of food in nickel utensils is regarded as safe. Nickel crucibles may be used for smelting minerals with potassium hydroxide, and small ones are suitable for determination of the volatile matter and ash of coal. It exhibits resistance to many corroding agencies, being unaffected, or nearly so, by many acids and alkalis, and is employed to a considerable extent in the latter industry. It is one of the strongest non-ferrous metals, and is far superior to brass for many applications. Edison predicted the future use of nickel one twenty-thousandth of an inch in thickness in place of paper, as it takes printers' ink to better effect. See "Nickel and Corrosion-Resisting Nickel Alloys," by R. J. McKay (*Ind. Eng. Chem.*, **28**, 1391 (1936)).

For use as a catalyst the metal is prepared by heating the hydrated oxide, carbonate, formate, or oxalate at from 250° to 300° C. in the absence of air, although when obtained by reduction it is liable to contain some unstable hydrides. When used in connection with the hydrogenation of oils, it can be regenerated by removing the oil with a solvent, then treating the catalyst with some agent capable of dissolving the film of oxide on the metal, washing, and sealing it against access of air.

Nickel forms three **oxides**: (1) monoxide ( $\text{NiO}$ ), a green powder, obtained by heating the hydroxide, or carbonate; (2) trinickel tetroxide ( $\text{Ni}_3\text{O}_4$ ), a grey powder, made by heating nickel chloride in a current of oxygen at 400° C.; (3) sesquioxide ( $\text{Ni}_2\text{O}_3$ ), a black powder, obtained by heating nickel nitrate to decomposition.

**Nickel hydroxide** ( $\text{Ni}(\text{OH})_2$ ) is obtained as a light green precipitate by adding an alkaline solution to a solution of a soluble nickel salt.

The **chloride** ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ), used in the preparation of sympathetic ink, etc., **nitrate** ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ), and **sulphate** ( $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ ) which crystallizes in prisms, are all green in colour and soluble in water. The sulphate is used as a mordant.

Several **sulphides** are known; of these, nickel monosulphide ( $\text{NiS}$ ) is black and insoluble in water and dilute acids.

The **carbonate** ( $\text{NiCO}_3$ ) (a crystalline compound insoluble in water)

occurs in nature as the mineral *zaratite*. The **cyanide** ( $\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$ ) (which is insoluble in water), the nitrate, the sulphate, the double nitrate of nickel and ammonium, and the double sulphate of nickel and ammonium ( $\text{NiSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ) (which are soluble in water), and the fluoride are all used in nickel-plating.

The compounds of nickel impart a reddish-yellow colour to a fused bead of borax, and some are used in the ceramic industries, the monoxide imparting a delicate brown colour to pottery. (See Alloys, and "Monel Metal".)

**NICOTINAMIDE** (Nicotinic Acid Amide, Niacin Amide) ( $\text{C}_6\text{H}_6\text{ON}_2$ ) — A white, crystalline, almost odourless powder, namely, pyridine-3-carboxylic acid amide; very soluble in water and alcohol; slightly soluble in ether; m.p.  $128^\circ$  to  $131^\circ$  C. Nicotinamide is the pellagra-preventing factor, isolated from the vitamin B complex, but now prepared synthetically by treating nicotinic acid with sulphonyl chloride and the action of ammonia on the resulting acid chloride. (See Vitamins (Vitamin B complex).)

**NICOTINE** ( $\text{C}_{10}\text{H}_{14}\text{N}_2$ ) — An oily, colourless liquid alkaloid of sp. gr. 1.009 and b.p.  $247^\circ$  C., constituting the principal alkaloid of tobacco (*Nicotiana tabacum* and *N. rustica*). The ordinary tobacco of commerce contains from 2 to 8 per cent. of the alkaloid, while the coarser *rustica* species frequently has a higher nicotine content.

Nicotine is miscible with water in all proportions at temperatures below  $60^\circ$  C., and is soluble in alcohol and ether. It is prepared from tobacco waste-stems, midribs, and damaged leaves—by treatment of the plant material with alkaline solutions, followed by steam distillation. It forms salts with acids readily, and the greater part of the nicotine sold is in the form of the sulphate, containing 40 per cent. of the alkaloid. When exposed to light nicotine becomes dark brown in colour, the colour increasing with age.

Nicotine is used mainly as an insecticide against soft-bodied insects, such as aphids. It is highly toxic to all animals and is one of the most poisonous of the alkaloids. It can be absorbed through the skin, and fatalities have resulted from the accidental spilling of concentrated solutions on clothing. When applied as sprays to fruits and vegetables, it is rapidly decomposed, and retains its insecticidal action for only a short time. It may be adsorbed tenaciously by clays, and "fixed nicotine" preparations of this sort are useful as insecticides over longer periods. Other insoluble compounds of nicotine have been proposed as insecticides, but none of these has been widely used.

See Landmark (*Chem. et Ind.*, 57, 172 (1947); Jackson (*Chem. Revs.*, 29, 123 (1941)); *Chemistry of Insecticides and Fungicides*, by D. E. H. Frear (D. Van Nostrand Co., New York); *Insecticides, and Tobacco*.

**NICOTINIC ACID** — See Vitamins.

**NIELLO-WORK** — Ornamented silver and gold plates, the engravings on same being filled up with a black composition such as silver sulphide.

**NIGROSINES** — A class of black dyes prepared by heating aniline and its hydrochloride with nitrobenzene and a metal. They are of various solubilities, some in water, some in alcohol, and others in oil, and are used in making shoe polishes, varnishes, inks, and in the dyeing and leather trades.

**NIKETHAMIDE** ("Anacardone," "Coramine," "Corvotone," "Nicamide," "Elitone") ( $C_{10}H_{14}ON_2$ ) — A colourless or faintly yellow, crystalline solid or oily liquid, being the diethylamide of pyridine-3-carboxylic acid,  $CH.N : CH.CH : CH.C.CO.N : (C_2H_5)_2$ ; prepared by

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treating nicotinic acid with thionyl chloride and the action of diethylamine on the resulting acid chloride; miscible with water in all proportions; soluble in alcohol, ether, and acetone; f.p.  $22^\circ$  to  $24^\circ$  C. Nikethamide has a stimulant action on the respiratory and vasomotor centres of the brain, increasing the depth and frequency of respiration, raising the blood pressure, and increasing the supply of blood to the heart. It is used in medicine as a stimulant in narcotic poisoning and post-operative collapse. In larger doses, it has also been used for the convulsant treatment of schizophrenia. It is administered as a solution containing 25 per cent. of nikethamide.

**NILE BLUE** — An oxazine dyestuff.

**NIOBE ESSENCE** — See Methyl Benzoate, and Perfumes.

**NIOBITE** — See Columbite.

**NIOBIUM** (Nb) — See Columbium. The International Union of Chemistry has accepted (1949) the name niobium for Element 41 instead of columbium.

**NITON** — See Radon.

**NITRAMINES** (Nitroamines) — Amines containing a nitro group attached to the nitrogen atom, having the general character expressed by  $R-NH-NO_2$ , such as phenylnitramine ( $C_6H_5.NH.NO_2$ ) and methyl-nitramine ( $CH_3.NH.NO_2$ ).

"**NITRAMON**" (Du Pont) — Trade-mark for an ammonium nitrate base blasting agent that is not detonated by sledge-hammer blows, impact of rifle bullets, or blow torches. Used for blasting in quarries and stripping.

**NITRANILINES** ( $C_6H_4(NH_2)(NO_2)$ ) — There are three of these compounds (*ortho*, *meta*, and *para*). The *ortho* and *para* isomers are produced by nitration of aniline following upon acetylation and followed by hydrolysis; the *meta* compound is obtained by partial reduction of *m*-dinitrobenzene by means of ammonium sulphide. All are yellow, crystalline, and readily soluble in alcohol, melting respectively at  $71.5^\circ$ ,  $114^\circ$ , and  $146^\circ$  C. The *para* compound is used in making *para*-nitraniline red.

There are also di- and tri-nitranilines, the tri- compound ( $C_6H_4(NH_2)_3$ ) ( $NO_2$ )<sub>3</sub> (2, 4, 6) being the yellow crystalline body known as picramide, m.p.  $188^\circ$  C., and hydrolysable by alkali to picrate, which yields picric acid upon acidifying.

**NITRATES** — See Chemical Compounds, and Nitrogen Compounds.

**NITRATION** — A term given to the process by which, using generally strong nitric acid or a mixture of that acid with concentrated sulphuric acid, the nitro group ( $-\text{NO}_2$ ) is introduced into organic compounds, as illustrated by the production of nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ) and dinitrobenzene ( $\text{C}_6\text{H}_4(\text{NO}_2)_2$ ) from benzene ( $\text{C}_6\text{H}_6$ ). Again, toluene ( $\text{CH}_3\cdot\text{C}_6\text{H}_5$ ) can, by the action of strong nitric acid, be converted successively into mononitrotoluene ( $(\text{CH}_3)\text{C}_6\text{H}_4(\text{NO}_2)$ ), dinitrotoluene ( $(\text{CH}_3)\text{C}_6\text{H}_3(\text{NO}_2)_2$ ), and trinitrotoluene ( $(\text{CH}_3)\text{C}_6\text{H}_2(\text{NO}_2)_3$ ). (See "Nitration," by H. McCormack (*Ind. Eng. Chem.*, **29**, 1333 (1937)) ; *Unit Processes in Organic Chemistry*, by P. H. Groggins (McGraw-Hill Book Co., New York) ; Explosives.)

**NITRE** — See Potassium Compounds.

**NITRE CAKE** — See Sodium Compounds.

**NITRIC ACID** — See Nitrogen Compounds, and Nitrogen Fixation.

**NITRIC ETHER** — See Esters (Ethyl Nitrate).

**NITRIDES** — Boron, magnesium, lithium, silicon, titanium, and some other elements combine with nitrogen at a red heat to form nitrides, and these are decomposed by the agency of steam, thus yielding ammonia. Some can be obtained by passing ammonia gas over the metals heated in porcelain tubes to from  $400^\circ$  to  $800^\circ\text{C.}$ , which effects the decomposition of the ammonia.

The nitrides  $\text{TiN}$ ,  $\text{VN}$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{BN}$ ,  $\text{LaN}$ ,  $\text{ZrN}$ ,  $\text{ScN}$ ,  $\text{NbN}$ , and  $\text{ErN}$  have all been obtained by heating the corresponding oxides with the calculated weight of carbon to  $1,250^\circ\text{C.}$  in an atmosphere of nitrogen. Aluminium nitride is now an article of some commercial importance. An iron nitride ( $\text{Fe}_4\text{N}_2$ ) is formed when an arc, using a current of 3 to 10 amperes at 35 volts, is struck between iron electrodes in a quartz bulb in an atmosphere of nitrogen. (See Abrasives, and Aluminium.)

**NITRIFICATION** — A process by which ammonia and other nitrogenous organic substances present in soil are converted into nitrates by the action of micro-organisms. Ammonium carbonate, for example, is first of all oxidized and converted into a nitrite by the agency of micro-organisms of one kind, and this is changed by another class of micro-organisms into the state of nitrate, the process requiring the presence of a base. It is known that the presence of calcium sulphate (gypsum) greatly facilitates the nitrification of urine.

Nitrifying micro-organisms exist to a depth of about 6 feet in soil and are most active between  $12^\circ$  and  $37^\circ\text{C.}$ , but nitrification is practically confined to the surface, air being essential. The purification of sewage by filtration through soil is largely due to this process.

It has been demonstrated that one part of boric acid in two and a half million parts of nutrient solution greatly increases the activity of the bacteria which fix atmospheric nitrogen.

Bacterial denitrification is said to be a process of the reduction of nitrates in anaerobic conditions, the necessary energy being supplied by the oxidation of organic matter. (See Bacteria, Sewage, and Soil.)

**NITRILES (Alkyl Cyanides)** — Compounds containing the monovalent group—CN; they may be viewed as derivatives of hydrocyanic acid, the hydrogen in the HCN being replaced by radicals—for example, acetonitrile or methyl cyanide ( $\text{CH}_3\text{.CN}$ ), of b.p.  $82^\circ\text{C}$ ., sp. gr. 0.783 at  $20^\circ\text{C}$ .; ethyl cyanide ( $\text{C}_2\text{H}_5\text{.CN}$ ), of b.p.  $97^\circ\text{C}$ ., sp. gr. 0.783 at  $20^\circ\text{C}$ .; phenyl cyanide ( $\text{C}_6\text{H}_5\text{.CN}$ ), of b.p.  $191^\circ\text{C}$ ., sp. gr. 1.001 at  $25^\circ\text{C}$ .; and benzyl cyanide ( $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ ), of b.p.  $233^\circ\text{C}$ ., sp. gr. 1.018 at  $20^\circ\text{C}$ .

**NITRITES** — See Chemical Compounds, and Nitrogen Compounds.

**NITRO** — The univalent group  $\text{—NO}_2$ .

**NITROBENZENE (Oil of Mirbane)** ( $\text{C}_6\text{H}_5(\text{NO}_2)$ ) is a yellowish liquid of sp. gr. 1.205, m.p.  $5.6^\circ\text{C}$ ., and b.p.  $211^\circ\text{C}$ ., and is prepared from benzene by the action of a mixture of sulphuric and nitric acids. It may be distilled without decomposition, and has an intense odour of bitter almonds. It is miscible with alcohol and ether, and used in the preparation of aniline and dyes. It is extremely toxic, and fatal accidents have been known where it was mistaken for benzaldehyde.

There are three dinitrobenzenes ( $\text{C}_6\text{H}_4(\text{NO}_2)_2$ ) and three trinitrobenzenes ( $\text{C}_6\text{H}_3(\text{NO}_2)_3$ ). *Meta*-dinitrobenzene (1, 3) is an almost colourless solid, of m.p.  $90^\circ\text{C}$ ., and formed by the action of nitric acid and less nitrobenzene.

**NITRO-CALCITE** — Native calcium nitrate.

**NITROCELLULOSE (Nitro-Cotton, Cellulose Nitrate)** — The reaction of cellulose ( $(\text{C}_6\text{H}_{10}\text{O}_5)_n$  or  $\text{C}_6\text{H}_7\text{O}_2(\text{OH})_3$ ) with nitric acid in the presence of sulphuric acid (using, for example, an excess amount of "mixed acid" containing  $\text{HNO}_3$  25 per cent.,  $\text{H}_2\text{SO}_4$  55 per cent.,  $\text{H}_2\text{O}$  20 per cent.) at a controlled temperature ( $20^\circ$  to  $40^\circ\text{C}$ .) produces in approximately 30 minutes with vigorous agitation nitrocellulose, or more correctly cellulose nitrate, which is an ester. The desired degree of nitrogen content attained in the product is determined by the variation of the above factors, since various applications require different nitrogen content. The principal products are:

13.5 to 12.5 per cent. N for smokeless powder;

12.2 to 11.8 per cent. N for lacquer and film;

11.7 to 11.2 per cent. N for lacquer;

11.2 to 10.7 per cent. N for plastic, especially celluloid with addition of camphor for plasticizer.

The solubility of these various types is an important property in practice, being closely related to their applications, thus, 13.5–12.5 per cent. is soluble in acetone or esters; 12.2–11.8 per cent. in acetone, ether–alcohol mixture, ethyl acetate, butyl acetate, or amyl acetate, and the ester solvents permit the addition of various amounts of hydrocarbons; 11.7–11.2 per cent. in methanol, ether–alcohol mixture or ester–hydrocarbon mixtures; and 11.2–10.7 per cent. in ethanol–toluene mixture; some of the lower nitrogen content are soluble in ethanol. The "solubility" of these materials is actually a peptizing (colloidal) effect rather than one of true solution.

Nitrocellulose of low viscosity, which is desired for lacquers that are

applied by spray-gun, is produced by heating the original product with water under pressure. The addition of such solvents as acetone or ethyl acetate decreases the viscosity, whereas benzene increases this. The viscosity is determined by observing the time of fall, say one-half second, of a steel sphere of specified diameter ( $\frac{5}{16}$  inch) and mass (2.043 grams) through a definite depth (10 inches) of the liquid maintained at a definite temperature (25° C.). In contrast to such a low-viscosity nitrocellulose, a similarly prepared solution—except only the quality of the nitrocellulose—might require as much as 20 seconds, this being a high viscosity value.

The cellulose used may be cotton linters, alpha-cellulose from wood pulp, or straw pulp. Schur and Hoos ("Nitration of Purified Wood Fibre," *Ind. Eng. Chem.*, **29**, 26 (1937)) state that "so-called half-second nitrocellulose of excellent quality may be prepared direct by the nitration of pretreated sheets of wood pulp." The following comparative results are also presented by them :

	urified Wood Pulp	Purified Cotton Linters
Alpha-Cellulose, per cent. . . . .	94.8	99.2
Yield upon Nitration, per cent. . . . .	150	157
Colour of Nitrocellulose Solution (Standard KI—I <sub>2</sub> ) . . . . .	22	19

(See Celluloid, Collodion Cotton, Explosives, Lacquers, and Pyroxylin.)

**"NITRO-CHALK"** — A fertilizer consisting of ammonium nitrate and dried Billingham calcium carbonate, containing  $15\frac{1}{2}$  per cent. of nitrogen, of which it has been alleged that one half is in the nitrate form and the other half in ammoniacal form. (See Nitrogen Fixation.)

**NITROCHLOROBENZENE** (*ortho*, *meta*, and *para*) ( $C_6H_4Cl(NO_2)$ ) — Crystalline intermediates soluble in alcohol and ether, and of melting points, 32.5°, 44°, and 83° C., respectively.

**NITROGEN (N) and its Compounds** — Atomic weight 14.008. See Elements for other data ; and also accompanying Chart. Nitrogen is contained in the air, of which it constitutes about four-fifths, the amount being estimated at approximately 30,000 tons over every acre of land and sea. In combination, it occurs as crude sodium nitrate ( $NaNO_3$ ) in Chile nitre (Chile saltpetre) found in Chile, Peru, and elsewhere, and is largely employed as a nitrogenous fertilizer. It is also found in combination as potassium nitrate in the form of *nitre* or saltpetre ( $KNO_3$ ) in certain soils in India and Ceylon, and is a constituent of many animal and vegetable substances.

It is produced commercially by the liquefaction of air and boiling off the nitrogen at  $-195.8^\circ$  C.; while by the "Borsig" process methane is burned in air, thus producing carbon dioxide (which is absorbed under pressure in water) and dry nitrogen of 99 per cent. purity. As thus made it is used in the manufacture of calcium cyanamide and synthetic ammonia. (See Coke Ovens (Gas), Oxygen, and Nitrogen Fixation.)

# NITROGEN-CONTAINING SUBSTANCES CHART SHOWING PRINCIPAL INTER-RELATIONSHIPS

Arrangement Based on Valency and Reduction-Oxidation Properties.

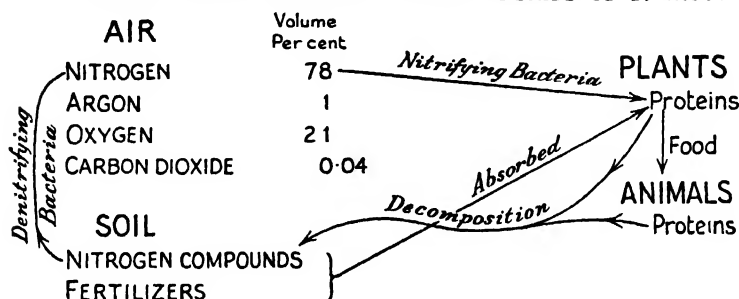
Arranged by the Editor.

Ammonia NH <sub>3</sub>	Hydrazine H <sub>2</sub> N.NH <sub>2</sub>	Hydroxylamine H <sub>2</sub> NOH	Nitrogen N	Nitric Oxide NO	Nitrous Acid HNO <sub>2</sub>	Nitric Acid HNO <sub>3</sub>
					Nitrogen Trioxide N <sub>2</sub> O <sub>3</sub>	Nitrogen Pentoxide N <sub>2</sub> O <sub>5</sub>
				Nitrous Oxide N <sub>2</sub> O	Nitrogen Tetroxide N <sub>2</sub> O <sub>4</sub>	Nitrogen Dioxide NO <sub>2</sub>
			Hydrazoic Acid HN <sub>3</sub>	Hyponitrous Acid HON.NOH		
Ammonia Compounds INORGANIC NH <sub>4</sub> OH NH <sub>4</sub> Cl NH <sub>4</sub> Na; Mg <sub>2</sub> N <sub>3</sub> NH <sub>4</sub> Cl ORGANIC CH <sub>3</sub> .NH <sub>2</sub>	Hydrazine Compounds INORGANIC N <sub>2</sub> H <sub>4</sub> .2HCl N <sub>2</sub> H <sub>4</sub> .HCl ORGANIC C <sub>6</sub> H <sub>5</sub> HN.NH <sub>2</sub>	Hydroxylamine Compounds INORGANIC H <sub>2</sub> NOH.HCl H <sub>2</sub> NONa ORGANIC C <sub>6</sub> H <sub>5</sub> H.NOH	Hydrazoic Azides NaN <sub>3</sub> ORGANIC CH <sub>3</sub> N		Nitrites INORGANIC NaNO <sub>2</sub> ORGANIC CH <sub>3</sub> .ONO Nitroso- Comp. C <sub>6</sub> H <sub>5</sub> .NO	Nitrates INORGANIC NaNO <sub>3</sub> ORGANIC CH <sub>3</sub> .ONO <sub>2</sub> Nitro-Comp. C <sub>6</sub> H <sub>5</sub> .NO <sub>2</sub>
				Oxyazo-Comp. C <sub>6</sub> H <sub>5</sub> N.NC <sub>6</sub> H <sub>5</sub> O		Of Compound Displayed
				Diazo-Comp. C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> Cl C <sub>6</sub> H <sub>5</sub> N <sub>2</sub> OH		Explosives : Certain Organic Nitrates Certain Nitro- Compound Certain Fulminates and Azides
Pyrrole CH : CH.CH : CH.NH						
Pyridine CH.CH.CH.CH.CH N						
	Aryl Hydrazines of aldehydes of ketones	Oximes of aldehydes of ketones				
Ammonium Salts of Carboxylic Acids CH <sub>3</sub> .COONH <sub>4</sub>						
Amides CH <sub>3</sub> .CONH <sub>2</sub>						
Aminoacids CH <sub>3</sub> .NH <sub>2</sub>						
COOH						
Proteins						
Hydrocyanic Acid HCN						
Cyanogen NC.CN						
Cyanides NaCN CH <sub>3</sub> .CN						
Isocyanides CH <sub>3</sub> .NC						
Cyanates NH <sub>4</sub> .NCO						
Fulminates Hg(ONC) <sub>2</sub>						
Urea OC(NH <sub>2</sub> ) <sub>2</sub>						
						Foods : Proteins
						Dyes : Azo-com- pounds

" Nitrogen is the most versatile form of  
elemental matter" (M. O. Forster).

Nitrogen can be readily made in the laboratory from the air by abstraction of the oxygen, for example, by the use of alkaline potassium pyrogallate solution, which speedily absorbs oxygen from air confined in a closed vessel, and leaves the nitrogen unabsorbed. Similarly, when phosphorus is burned in air it combines with the oxygen to form phosphorus pentoxide, leaving nearly pure nitrogen; and cuprous salt solutions either in hydrochloric acid or in ammonium hydroxide likewise serve to remove the oxygen of air and to leave the nitrogen. It can also be made by passing a stream of air over metallic copper heated to redness, when the oxygen of the air combines with and is fixed by the copper, forming cupric oxide, nitrogen gas passing over. Ammonium dichromate, when heated, yields nitrogen gas with considerable violence.

DIAGRAM SHOWING SELECTED RELATIONSHIPS OF NITROGEN



Every living thing contains nitrogen element, which when free and pure is a colourless gas without taste or smell, nearly insoluble in water (1 volume of which at 0° C. dissolves only 0.0235 volume of the gas), and is in this state a very inert chemical substance exhibiting but little tendency to enter into chemical combination with other substances. It can, however, be prepared in a much more chemically active (therefore probably allotropic) form by an electrical process. A corona discharge at 20,000 volts from a fine wire is stated to be capable of transforming 4 per cent. pure nitrogen into an activated form, in which state it readily effects the decomposition of hydrocarbons, combines with hydrogen to form ammonia, combines with oxygen to form oxides, and with various metals to form nitrides. It is more stable than activated hydrogen, and persists for some hours, exhibits a glow, and attacks acetylene and other gases containing carbon, thus producing cyanogen compounds. Evidence has also been obtained that nitrogen may be chemically active and yet show no luminosity.

The consumption of nitrogen in its various forms for fertilizing purposes in the United Kingdom and Ireland is estimated at about 6½ pounds per acre of arable land.

The following figures are offered, through the courtesy and with the permission of British Sulphate of Ammonia Federation, Limited, as fair estimates of the world's production and consumption of fixed Nitrogen in recent years.

**FERTILIZER NITROGEN, WORLD PRODUCTION AND CONSUMPTION  
FOR THE PERIODS SHOWN**

Courtesy of British Sulphate of Ammonia Federation, Limited  
Data arranged by the Editor.

Country	Metric Tons Nitrogen Annual Average for the two-year period 1937-1939		Metric Tons Nitrogen For the one-year period 1949-1950	
	Production	Consumption	Production	Consumption
United Kingdom ..	131,500	68,000	362,000	276,000
France .. .. .	149,500	179,500	234,000	250,000
Belgium .. .. .	83,500	54,000	183,000	85,000
Netherlands .. ..	105,000	90,500	114,000	146,000
Norway .. .. .	85,000	10,500	153,000	42,000
Remainder of Europe, exclusive of U.S.S.R.	1,014,000	1,000,500	—	—
U.S.S.R. not reported ..	—	—	—	—
Italy .. .. .	—	—	137,000	139,000
Germany, Western Zones	—	—	497,000	368,000
Remainder of Europe, inclusive of U.S.S.R. and Germany, Eastern Zone .. .. .	—	—	746,000	903,000
U.S.A. .. .. .	187,000	330,000	1,328,000	1,176,000
Canada .. .. .	50,500	10,000	190,000	43,000
Chile .. .. .	225,000	5,000	271,000	14,000
Remainder of North and South America ..	1,000	31,000	3,000	63,000
Japan .. .. .	421,000	437,000	386,000	442,000
China .. .. .	1,000	29,000	10,000	59,000
India-Ceylon .. ..	5,000	28,000	11,000	86,000
Remainder of Asia, ex- clusive of U.S.S.R. ..	—	43,000	62,000	152,000
Egypt .. .. .	—	77,000	—	96,000
Remainder of Africa ..	—	19,000	18,000	53,000
Australasia .. ..	5,500	14,500	12,000	23,000
WORLD, exclusive of U.S.S.R. .. ..	2,464,500	2,426,500	—	—
WORLD TOTAL .. ..	—	—	4,717,000	4,416,000

**Ammonia** ( $\text{NH}_3$ ) — One of the most important compounds of nitrogen is ammonia, the salts of which are largely obtained from the *ammoniacal liquor* of gasworks, for which purpose the gas liquor is treated with lime and distilled, the ammonia being thus driven over and condensed in water, or passed into sulphuric or hydrochloric acid, forming respectively ammonium sulphate  $((\text{NH}_4)_2\text{SO}_4)$ , or chloride ( $\text{NH}_4\text{Cl}$ ). Cobb's process for recovering ammonia from coal consists in washing the gas in a solution of zinc sulphate, thus causing the precipitation of zinc sulphide, accompanied with the production of ammonium sulphate in solution. The zinc sulphide is filtered off and roasted, thus producing the oxide and sulphur dioxide gas, and by suspending the oxide in water and exposing it to the roaster gas, zinc sulphate is regenerated for use over again. The ammonium sulphate is recovered from its solution by evaporation.

Pure (liquefied) ammonia boils at  $-33.4^\circ \text{C.}$ , can be thermally decomposed into hydrogen and nitrogen by exposure to various surfaces at temperatures ranging from  $631^\circ$  to  $1,215^\circ \text{C.}$ , and is very soluble in water, which, at the ordinary temperature of the air, absorbs 727 times its own volume of the gas, and at  $0^\circ \text{C.}$  1,148 volumes. The solution is colourless, strongly alkaline, and of characteristic pungent odour. A solution containing 35 per cent. of ammonia gas dissolved in water, having a sp. gr. of 0.882 at  $15^\circ \text{C.}$ , is known as *liquor ammoniacæ*, and it is also marketed of sp. gr. 0.920 of 22 per cent. ammonia.

As a solvent for salts it resembles water more closely than any other substance. The alkali metals dissolve in liquid ammonia yielding blue solutions of high electrical conductivity, the blue colour being due to solvated electrons ( $e^-$  ammoniated). The metal ion formed at the same time, e.g.,  $\text{Na}^+$ , is colourless in ammonia. The alkaline-earth metals are soluble but to a smaller extent than the alkali metals.

Ammonia is produced on a commercial scale from a mixture of nitrogen and hydrogen gases contained under pressure and exposed to a high temperature, using a catalytic agent to effect the combination. This and some other processes of production are described under the heading of Nitrogen Fixation. The "Bucher" process attracted attention at one time. It is conducted by passing nitrogen through a heated mixture of coke, soda-ash, and iron compounded in the form of briquettes; sodium cyanide is thus produced, and this, when hydrolysed by steaming, yields ammonia.

The cyanamide process for the production of ammonia is referred to elsewhere. (See Cyanamide.)

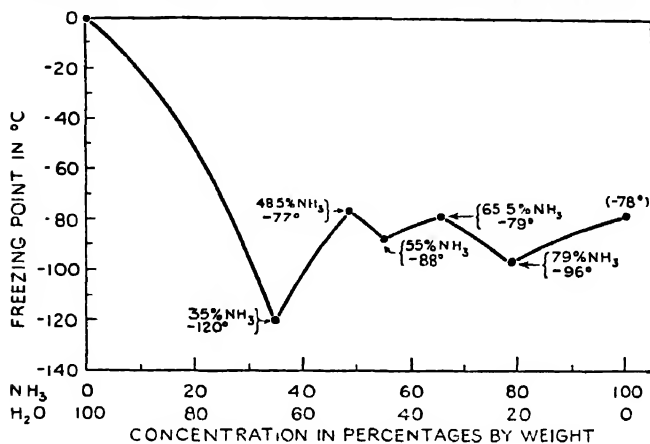
As produced by any of these processes, ammonia can be oxidized to make nitric acid, or converted into sulphate, phosphate, or other salts. The essential sources are gasworks, coke-ovens, gas producers, shaleworks, ironworks, and bone and other carbonizing works, and synthetic ammonia.

Ammonia is extensively and variously used as a detergent, saponifying agent, in electrodeposition baths, and in connection with refrigerating appliances, while some of its salts are employed for rendering wood and other materials non-flammable. It is used for treating water in

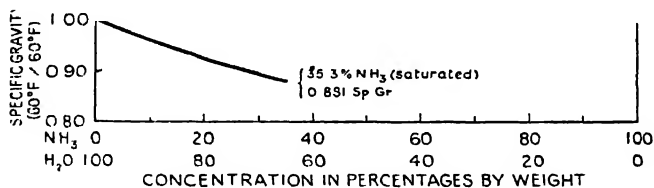
## NITROGEN

 $\text{NH}_3\text{--H}_2\text{O}$  MIXTURES

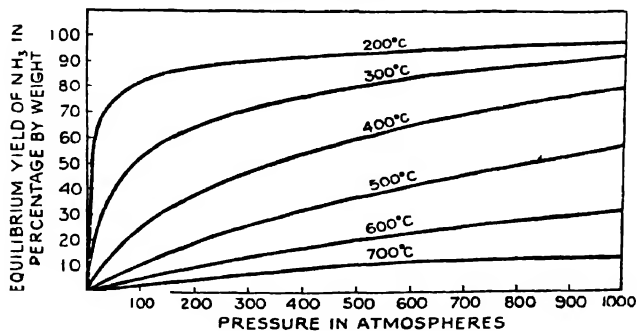
## FREEZING POINT—CONCENTRATION RELATIONSHIP

 $\text{NH}_3\text{--H}_2\text{O}$  MIXTURES

## SPECIFIC GRAVITY—CONCENTRATION RELATIONSHIP

 $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$  REACTION

## EQUILIBRIUM CONCENTRATION—TEMPERATURE—PRESSURE RELATIONSHIP



association with chlorine, chloramine being thus formed and neutralizing any excess of chlorine used for its purification. Cracked ammonia as a source of hydrogen, and made by passage of ammonia gas over a heated catalyst, is used in welding metals, and ammonia itself can be employed for nitriding steel and thus hardening it. (See Coal, and Nitrogen Fixation.)

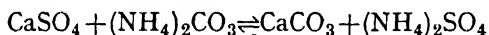
Ammonia is the simplest form of the class of bodies described as amines, and is in fact the prototype of the organic bases.

The hypothetical ammonium radical ( $\text{NH}_4$ ) capable of replacing an atom of hydrogen in acids is known in ammonium amalgam made by electrolysis of ammonium salts solutions using a mercury cathode with cooling.

**Ammonium Sulphate** ( $(\text{NH}_4)_2\text{SO}_4$ ) is a white soluble salt, and constitutes an efficient weed-killer for weeds which do not grow in an acid soil, while it is also largely used as a nitrogenous fertilizer and for the manufacture of ammonium alum (see Alums) and other compounds.

Ammonium sulphate is produced industrially by neutralization of ammonia and sulphuric acid, and subsequent evaporation and crystallization. The principal sources of the ammonia are coke ovens, and synthetic ammonia.

There is a process for obtaining this salt by treating very finely divided gypsum with ammonium carbonate, when, owing to the smaller solubility of calcium carbonate than that of calcium sulphate, reaction occurs, producing ammonium sulphate and calcium carbonate. The reaction is a so-termed reversible one—



In one method of procedure calcium sulphate suspended in a solution of ammonia is passed down a series of pipes carrying a current of carbon dioxide and steam in the opposite direction, resulting in the production of a mixture of calcium carbonate in 30 per cent. ammonium sulphate, 90 per cent. of the sulphuric acid being recovered from the gypsum. The calcium carbonate retains, after filtering, about 0.5 per cent. nitrogen and is useful as a low-grade fertilizer.

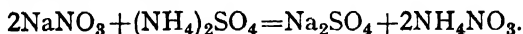
Another process consists in producing ammonium sulphite in such form that it is readily converted into sulphate by air. Ammonia vapour and water in vapour or fine spray form are caused to react with a mixture of sulphur dioxide gas and air in a chamber at just below  $100^\circ \text{C}$ ., by which means the sulphite is produced and precipitated, after which it is exposed in heaps or shallow deposits and raked from time to time, thus changing it to the sulphate.

The "Electro-Nitrogen" process, as developed by M. R. Tern, depends upon the interaction of ammonia vapour and sulphur trioxide (as made from sulphur dioxide gas in an electric arc) in an electrostatic precipitation plant in which the ammonium sulphate is separated. It is particularly directed to the recovery of sulphur from spent gas purifier material.

**Ammonium Persulphate** ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) is made by electrolysis of a solution of ammonium sulphate dissolved in dilute sulphuric acid

(1 part to 7 parts water) in a divided cell. It is soluble in water and used in electroplating, photography, etc. It has been reported as explosive under conditions causing oxidation of the ammonium radical, and particularly so if the salt comes into contact with organic matter.

**Ammonium Nitrate** ( $\text{NH}_4\text{NO}_3$ ) is a colourless salt of m.p.  $170^\circ\text{C}$ ., and as prepared from ammonia and nitric acid is used in the making of the explosive named "Roburite," and as a fertilizer. During World War I ammonium nitrate was produced by a process which consisted of the double decomposition of Chile saltpetre and ammonium sulphate as expressed in the equation :



Another process used during World War I consisted of passing carbon dioxide into strong ammonia liquor in a tower and introducing the carbonate thus formed into a solution of calcium nitrate, the precipitated calcium carbonate being removed by filtration, and the ammonium nitrate being subsequently crystallized from the resulting evaporated liquor. Direct neutralization of nitric acid by ammonia is practised with subsequent evaporation to the point where the solution, upon being sprayed into the top of high towers and encountering therein upward moving warm air, forms solid spheres, which do not "cake" on storing. (See "Properties of Granular and Monocrystalline Ammonium Nitrate," by W. H. Ross and others (*Ind. Eng. Chem.*, **37**, 1079 (1945) ; and Fertilizers).)

**Ammonium Chloride** ( $\text{NH}_4\text{Cl}$ ) — There are several processes of manufacture ; in one, ammonia gas is passed into hydrochloric acid. As manufactured by the reaction between ammonium sulphate and alkali chlorides, and as prepared from gas and other ammoniacal liquors by treatment with hydrochloric acid, it is subsequently purified by sublimation, and is a colourless, crystalline substance, soluble in cold water to the extent of about 33 per cent. of the solution. It is known commercially by the name of "sal-ammoniac." Its vapour appears to be completely dissociated into ammonia and hydrogen chloride at between  $200^\circ$  and  $400^\circ\text{C}$ .

Ammonium chloride is used in medicine, in dyeing operations, in electric batteries, as a fertilizer, in the tinning and soldering trades, in galvanizing, and in the preparation of a cement (made of iron filings mixed with 1 or 2 per cent. sulphur and moistened with a solution of the sal-ammoniac) for fixing iron in stonework.

There are two **carbonates**, the commercial article being made by heating a mixture of ammonium sulphate and ground chalk to redness and condensing the generated vapours, the product being a mixture of ammonium hydrogen carbonate or so-called bicarbonate ( $(\text{NH}_4)\text{HCO}_3$ ) and ammonium carbamate, from which the carbamate can be washed out with alcohol, and has a strong ammoniacal odour. **Ammonium Carbonate** ( $(\text{NH}_4)_2\text{CO}_3$ ) (the normal carbonate) can be obtained by passing ammonia gas (excess) into a strong solution of the commercial compound, when the carbamate becomes converted into the normal carbonate by the action of water, and the bicarbonate content

is also changed into the same product by the action of ammonia. Upon exposure to air it gives off ammonia and is changed back to the **bicarbonate** compound ( $\text{NH}_4\text{HCO}_3$ ), a body which, when crystallized in a pure, dry state, does not smell of ammonia. Ammonium carbonate is used as a fertilizer, in making smelling salts, and in a number of industries. (See Nitrogen Fixation.) **Sal-volatile** or aromatic spirit of ammonia is a solution of ammonium carbonate in ethyl alcohol containing free ammonia and flavoured with oils of lemon and nutmeg, and used in medicine as a stimulant.

**Ammonium Carbamate** ( $(\text{NH}_4\text{O})(\text{NH}_2)\text{CO}$ ) is a white, crystalline, volatile, and soluble powder described as the "anhydride" of ammonium carbonate, formed by the interaction of dry ammonia gas and carbon dioxide.

**Ammonium Chlorate** ( $\text{NH}_4\text{ClO}_3$ ), obtained by the addition of ammonium chloride to a solution of sodium perchlorate, is a colourless, soluble salt used in the manufacture of explosives.

**Ammonium Phosphate** ( $(\text{NH}_4)_2\text{HPO}_4$ ) — A white, crystalline salt, soluble in water, made by the interaction of ammonium hydroxide and phosphoric acid; used in medicine, fireproofing, etc. Electro-thermal processes are involved in the production of ammonium phosphate from calcium phosphate in France, and in the United States.

**Ammonium Sulphamate** (Du Pont) ( $\text{NH}_4\text{O}.\text{SO}_2.\text{NH}_2$ ) — A white, crystalline solid, soluble in water. Used for flameproofing textiles and paper.

**Ammonium Sulphide** ( $(\text{NH}_4)_2\text{S}$ ) — A yellow, crystalline substance, soluble in water and alcohol, used in the textile industry. The solutions obtained in water by the interaction of ammonium hydroxide and hydrogen sulphide are of indefinite constitution, and contain a number of sulphides. Ammonium sulphide vapour can be quantitatively transformed into ammonium sulphite and sulphate by atmospheric oxidation at  $450^\circ$  to  $650^\circ\text{C}$ . in presence of a suitable catalyst.

So-called ammonium polysulphide has been found useful as a fungicide for the control of apple, rose, and gooseberry mildews, its value being in relation to its polysulphide sulphur content, and its wetting and spreading properties. It is best used as a spray.

**Ammonium Disulphide** ( $(\text{NH}_4)_2\text{S}_2$ ) is generally obtained as a yellow oil by heating the pentasulphide; it sets on standing to a mass of lemon-yellow, needle-shaped crystals.

**Ammonium Pentasulphide** ( $(\text{NH}_4)_2\text{S}_5$ ) has been prepared by the action of sulphur on solutions of ammonium hydrosulphide in dry alcohol, and can be obtained in orange-yellow crystals.

**Ammonium Thiocyanate** (Sulphocyanate, Sulphocyanide, or Rhodanate) ( $\text{NH}_4\text{SCN}$ ) — A colourless, deliquescent, crystalline body, soluble in water and alcohol; marketed of 95 per cent. strength.

**Ammonium Chromate** ( $(\text{NH}_4)_2\text{CrO}_4$ ) and **Ammonium Dichromate** ( $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ ) are yellow and red, respectively, crystalline, soluble salts used as mordants. When heated, a moderately violent reaction occurs in which nitrogen gas is evolved, and green chromic oxide remains as a residue.

**Ammonium Bifluoride**  $((\text{NH}_4)\text{HF}_2)$  is a white, crystalline, soluble salt used in the ceramic industry and as a sterilizing agent in brewery work.

**Ammonium Tartrate**  $((\text{NH}_4)_2\text{C}_4\text{H}_4\text{O}_6)$  is a white, crystalline, soluble salt used in the textile industry.

**Ammonium Bitartrate**  $((\text{NH}_4)\text{H.C}_4\text{H}_4\text{O}_6)$  is a white, crystalline, soluble salt used in making baking-powders.

**Ammonium Bromide**  $(\text{NH}_4\text{Br})$  is a colourless, crystalline, soluble salt used in photography and medicine.

**Ammonium Oxalate**  $((\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O})$  is a colourless, crystalline, soluble salt frequently used as an analytical reagent.

**Ammonium Perchlorate**  $((\text{NH}_4)\text{ClO}_4)$  is a white, crystalline, soluble salt used in pyrotechnics and making explosives.

**Ammonium Phosphomolybdate**  $((\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 12\text{H}_2\text{O})$  is a yellow, crystalline, insoluble salt, the formation of which is a favourite analytical test for soluble phosphate.

**Ammonium Vanadate**  $(\text{NH}_4\text{VO}_3)$  is a white, crystalline salt, soluble in warm water, used as a mordant and in preparation of vanadium salts.

**Ammonium Acetate**  $(\text{NH}_4\text{C}_2\text{H}_3\text{O}_2)$ , **benzoate**  $(\text{NH}_4\text{C}_7\text{H}_5\text{O}_2)$ , **borate**  $((\text{NH}_4)_3\text{BO}_3)$ , **salicylate**  $(\text{NH}_4\text{C}_7\text{H}_5\text{O}_3)$ , **valerate**  $(\text{NH}_4\text{C}_5\text{H}_9\text{O}_4)$ , are all used medicinally. (See also Hydroxylamine, and Molybdenum (Ammonium Molybdate).)

**Nitrogen Oxides** — There are six of these, having the formulæ  $\text{N}_2\text{O}$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ , and  $\text{N}_2\text{O}_5$ ; and there are three acids corresponding respectively to the oxides:  $\text{N}_2\text{O}$ ,  $\text{N}_2\text{O}_3$ , and  $\text{N}_2\text{O}_5$ .

**Nitrous Oxide** ( $\text{N}_2\text{O}$ ), known also as laughing gas, can be obtained by heating ammonium nitrate to  $205^\circ\text{C}$ ., when it splits up into nitrous oxide and water:  $\text{NH}_4\text{NO}_3 = \text{N}_2\text{O} + 2\text{H}_2\text{O}$ , or by heating a mixture of sodium nitrate and ammonium sulphate to  $230^\circ\text{C}$ . and collecting the gas over mercury or water.

It is a colourless gas, soluble in water to the extent of 1.305 volumes in 1 volume of water at  $0^\circ\text{C}$ .; of a faint not unpleasant odour, and when breathed for a short time induces excitement and in some cases laughter. It is used to some extent as an anæsthetic in dentistry, and is easily liquefied to a colourless, mobile fluid which can be frozen solid. Liquid nitrous oxide boils at  $-89.5^\circ\text{C}$ . and solidifies at  $-102^\circ\text{C}$ . (See Hydrazoic Acids.)

**Nitric Oxide** ( $\text{NO}$ ) gas is generated by the action of nitric acid of sp. gr. 1.2 (32 per cent.) upon copper or mercury, when the nitrate of the metal passes into solution. It is colourless, and enters into combination with atmospheric oxygen to form red-brown, irritating, soluble vapours of nitrogen peroxide, a reaction which was originally used to test "the goodness of air." On the surface of heated platinum at  $1,000^\circ$  to  $1,500^\circ\text{C}$ . it is dissociated as follows:  $2\text{NO} = \text{N}_2 + \text{O}_2$ .

**Nitrogen Trioxide** ( $\text{N}_2\text{O}_3$ ) is made by exposing a mixture of nitric oxide and nitrogen dioxide to a temperature of  $-20^\circ\text{C}$ ., when it is produced as a bluish-green fluid. It forms nitrous acid with excess of cold water.

**Nitrogen Dioxide or Peroxide** ( $\text{NO}_2$ ) or **Tetroxide** ( $\text{N}_2\text{O}_4$ ) can be

prepared by passing a mixture of 2 volumes of nitric oxide with 1 volume of oxygen through a tube surrounded by a freezing mixture. At low temperatures it forms a colourless, crystalline compound,  $\text{N}_2\text{O}_4$ , which melts at  $-9^\circ\text{C}$ ., and at higher temperatures it takes on a yellow and then an orange colour. It boils at  $22^\circ\text{C}$ ., and gives off reddish-brown vapours; in fact, it is dissociated as the temperature rises, and at  $140^\circ\text{C}$ . it is entirely resolved into  $\text{NO}_2$ . (See "Absorption of Nitrogen Dioxide by Aqueous Solutions," by F. S. Chambers, Jr., and T. K. Sherwood (*Ind. Eng. Chem.*, **29**, 1415 (1937)).)

**Nitrogen Pentoxide** ( $\text{N}_2\text{O}_5$ ) is a white, solid, crystalline substance which melts at  $30^\circ\text{C}$ . with partial decomposition, and when suddenly heated, is apt to explode with violence, while in contact with water it produces nitric acid:  $\text{N}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{HNO}_3$ . It can be prepared by withdrawing the elements of water from nitric acid by means of phosphorus pentoxide:  $2\text{HNO}_3 + \text{P}_2\text{O}_5 = 2\text{HPO}_3 + \text{N}_2\text{O}_5$ , the mixture being cautiously made and kept cool at first, and then gently heated, when the  $\text{N}_2\text{O}_5$  distils over (b.p.  $47^\circ\text{C}$ .) and can be condensed in a refrigerated receptacle.

**Hyponitrous Acid** ( $\text{H}_2\text{N}_2\text{O}_2$ ) is an unstable substance, and has no present commercial importance. It can be treated to give water *plus* nitrous oxide, but is not reversely formed from nitrous oxide and water.

**Nitrous Acid** ( $\text{HNO}_2$ ) is not known in the pure state, but its salts, the **nitrites**, are stable compounds, and can be prepared by heating certain nitrates above their fusion-point, when oxygen is given off and the nitrites are obtained by this reduction; for example:



Most of the metallic nitrites are soluble in water, and when they are subjected to the action of dilute acids they are decomposed, brown vapours being given off, whereas the nitrates are stable under this treatment.

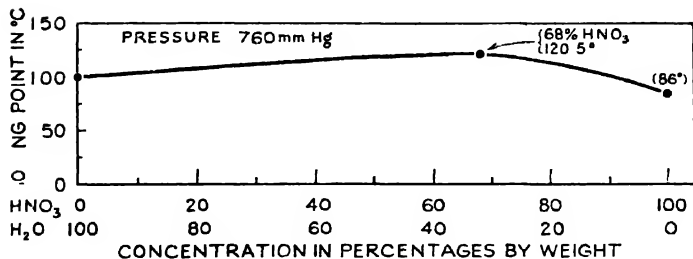
Nitrous acid (dilute) is a remarkable substance in that it is oxidized to nitric acid by manganese +7 ( $\text{KMnO}_4$  solution) in the presence of hydrogen ion; and reduced to nitric oxide by iodine +1 ( $\text{KI}$  solution) in the presence of hydrogen ion.

**Nitric Acid** ( $\text{HNO}_3$ ) is a very important compound, and is formed in a variety of ways, but the method by which it has in the past been mainly produced is by the action of sulphuric acid ( $\text{H}_2\text{SO}_4$ ) upon sodium nitrate ( $\text{NaNO}_3$ ). The first stage of the process is represented by the equation:  $\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_3$ , and by pushing the heating further there is a secondary change, as follows:  $\text{NaNO}_3 + \text{NaHSO}_4 = \text{Na}_2\text{SO}_4 + \text{HNO}_3$ , but the latter treatment causes some loss by decomposition of nitric acid. This operation is generally carried out in cast-iron eggs or cylinders lined with fire-clay, the nitric acid passing over in the form of vapour, which is condensed.

In practice, nearly equal parts of purified Chile nitrate and sulphuric acid are subjected to distillation, the strength of the acid which is employed depending upon the kind of nitric acid that is required, concentrated sulphuric acid of about  $160^\circ$  Twaddell being used for

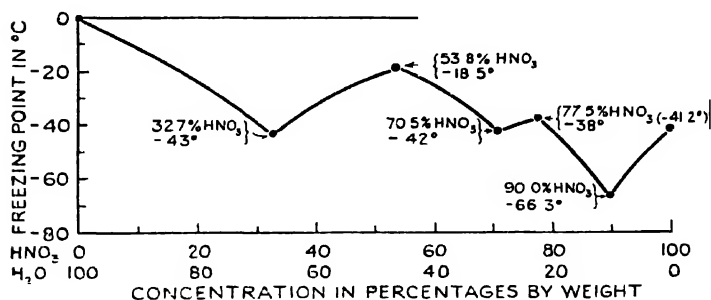
## HNO<sub>3</sub>—H<sub>2</sub>O MIXTURES

### BOILING POINT—CONCENTRATION RELATIONSHIP (PRESSURE CONSTANT)



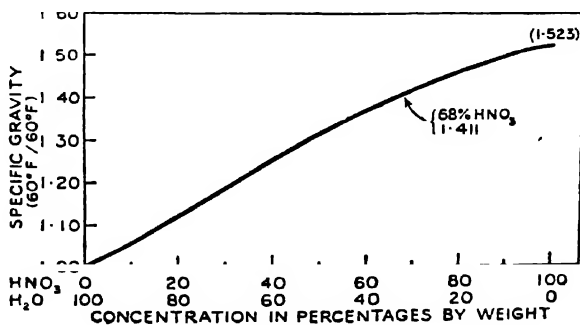
## HNO<sub>3</sub>—H<sub>2</sub>O MIXTURES

### FREEZING POINT—CONCENTRATION RELATIONSHIP



## HNO<sub>3</sub>—H<sub>2</sub>O MIXTURES

### SPECIFIC GRAVITY—CONCENTRATION RELATIONSHIP



making strong nitric acid, and that of about 140° Tw. (ordinary Glover tower acid) being used for production of weak nitric acid. Commercial grades of various strengths are made from 36° to 44° Baumé and 80° Tw., while so-called "aqua fortis" acid of 41½° Bé. contains 65-67 per cent. real  $\text{HNO}_3$ . (See Sodium (Hydrogen Sulphate).)

In the "Valentiner process" the decomposition of the sodium nitrate is effected in glass retorts *in vacuo*—that is, under reduced pressure—by which means the production of nitrous acid as an impurity is avoided, and there is no escape of acid fumes into the atmosphere. Nitric acid can now, however, be made more cheaply by oxidation of ammonia. (See Nitrogen Fixation.)

Nitric acid is colourless when pure, and is a strongly fuming corrosive liquid with a sp. gr. of 1.53, which attacks many metals with avidity and forms by combination therewith, or by reactions with their oxides or carbonates, a large number of corresponding nitrates. The so-called "fuming" nitric acid contains upwards of 86 per cent.  $\text{HNO}_3$ , and has a specific gravity of about 1.48. It is very corrosive, and in contact with many organic substances causes their combustion.

It is a powerful oxidizing and nitrating agent, and its uses in industrial chemistry are many and of great importance, including its employment in the manufacture of the explosives nitroglycerine, gun-cotton, etc. (See Explosives.)

Nitrates in the soil are produced by the slow oxidation of ammonia (derived from nitrogenous organic matter) in the presence of air and an alkali, and it has been conjectured that this process possibly accounts for the natural deposits found in Chile and elsewhere. (See *The Manufacture of Nitric Acid and Nitrates*, by A. Cottrell (Gurney and Jackson, London); Nitrification, and Nitrogen Fixation.)

**Nitrogen Trichloride** — Obtained from ammonium chloride by the action of chlorine ( $\text{NH}_4\text{Cl} + 3\text{Cl}_2 = \text{NCl}_3 + 4\text{HCl}$ ), nitrogen trichloride is a thin, oily, very volatile liquid of pale yellow colour and sp. gr. 1.65, having an irritating pungent odour. It is one of the most dangerous explosives, decomposing with great violence when exposed to sunlight or brought into contact with grease, turpentine, and many other substances.

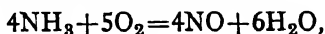
**Nitrogen Triiodide (Iodoazoimide, Monoammonate)** ( $\text{NH}_3\text{NI}_3$ ) is a crystalline body produced by addition of strong ammonia solution to powdered iodine and is also formed when dry ammonia acts on the less stable dibromoiodides.

**NITROGEN FIXATION** — The nitrogen fixation processes now operating are primarily used for the production of fertilizers, the surplus ammonia or nitric acid output being used for other purposes. Some of these processes depend upon the direct union of nitrogen with oxygen by gaseous explosion or under the influence of the electric arc (to which an extended surface is given) at a temperature of about 3,000° C., but this method can only be economically carried out where cheap and abundant supply of water-power is available for production of the requisite electric energy as in Norway.

It is stated that about 80 per cent. of the nitrogen oxide gases can be absorbed in water (forming nitric acid containing about 33 to 35 per cent  $\text{HNO}_3$ ), and, subsequently, some 15 per cent. in soda lye, forming sodium nitrite, which can be obtained in the solid form by evaporation. The dilute nitric acid can be concentrated up to about 68 per cent. by distillation under ordinary atmospheric pressure, while by distillation with concentrated sulphuric acid or in contact with fused sodium bisulphate the strength can be brought up to over 90 per cent.

In the "Häusser" process the heat caused by the explosion of a mixture of combustible gas (preferably coke-oven gas) and air is used to bring about the union of nitrogen and oxygen, oxides of nitrogen being produced which can be absorbed in water, whilst power is generated simultaneously. The nitrous gases are passed into vertical iron cylinders lined with acid-proof stone in which the nitric oxide is oxidized by atmospheric oxygen into nitrogen peroxide, the gases being finally condensed with water in washing towers and thus converted into nitric acid.

Nitric acid is also produced by the oxidation of ammonia, using catalytic agents, such as platinum gauze. In this process a mixture of air and ammonia containing about 10 per cent. of the latter, is passed through platinum gauze or other catalyst placed between washers of asbestos board or nickel-chrome sheet, heated at first to the required temperature, but maintained subsequently at a cherry-red heat by the chemical change which is involved, most of the nitrogen being oxidized to nitric oxide, which upon cooling combines with more oxygen to form nitrogen peroxide, and this is absorbed in water, forming nitric acid. Ammonia can thus be oxidized by air on the surface of a solid catalyst such as platinum wire gauze or ferric oxide at a temperature of about  $650^\circ$  to  $700^\circ \text{C.}$ , the ratio of ammonia to air being from 1 : 7 to 1 : 9, the main reaction being represented as follows :



the nitric oxide thus produced being converted into nitric acid by means of atmospheric oxygen and water ( $4\text{NO} + 3\text{O}_2 + 2\text{H}_2\text{O} = 4\text{HNO}_3$ ). For this purpose the gases issuing from the converter in which the nitric oxide is produced are cooled to about  $30^\circ \text{C.}$ , and then passed into the oxidation and absorption towers. The temperature at which oxidation begins depends to some extent upon the form of the platinum catalyst, namely, about  $145^\circ \text{C.}$  for corrugated platinum foil,  $170^\circ \text{C.}$  for crumpled foil pellets,  $240^\circ \text{C.}$  for wire gauze, and  $240^\circ \text{C.}$  for wire in plug form. The yield is negligible above  $900^\circ \text{C.}$

The crucial demand of this process for making nitric acid is obviously a supply of ammonia. The processes for producing ammonia from atmospheric nitrogen (used along with manufactured hydrogen) are now described. (Refer also to Nitrogen (Ammonia).)

The "Haber" synthetic ammonia process, which was in use in Germany before World War I, is based upon the direct union of nitrogen and hydrogen at a temperature of about  $600^\circ \text{C.}$ , maintained by means of an electric coil and under a pressure of from 200 to 300

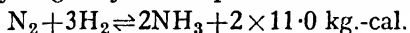
atmospheres, in the presence of a catalyst. The ammonia that is produced can be subsequently converted into nitric acid (by oxidation), ammonium nitrate, or ammonium sulphate. Metallic osmium serves well as a catalyst, but is too expensive for use on a manufacturing scale, and an activated iron catalyst such as ferromolybdenum is employed in practice. The U.S. Nitrogen Fixation Laboratory has found an excellent catalyst to be finely divided pure iron with an admixture of about 1 per cent. of aluminium oxide and 1 per cent. of potassium oxide.

As now worked on the "Haber-Bosch" principle at Billingham, the carbon monoxide of water-gas is made to react catalytically with steam so as to produce hydrogen. After compression and purification a mixture containing three volumes of hydrogen and one of nitrogen is made to produce ammonia by catalytic action at a relatively high temperature. The ammonia is dissolved in water and combines with a portion of the carbon dioxide (removed in the previous purification processes), and the ammonium carbonate thus produced is then made to react with anhydrite to produce ammonium sulphate and chalk. The chalk is utilized in making "nitro-chalk."

In the "Casale" process, as conducted in Italy, a pressure of from 700 to 850 atmospheres is used and the hydrogen is obtained electrolytically from large cells of a new type operated from hydro-electric currents obtained from great waterfalls. Some of this hydrogen is burnt with air, and thereby the required mixture of hydrogen and nitrogen is produced.

In the "Claude" process, nitrogen boiled off from liquefied air is admixed with hydrogen gas in suitable proportions, and the mixed gases subjected as in the "Haber" process, but under a greatly increased pressure, about 800 to 1,000 atmospheres, or nearly 6 tons per square inch, and at a temperature of 600° C., so that whereas in the "Haber" process only about 13 per cent. of the gases is transformed into ammonia, 42 per cent. transformation is effected, and the product is obtained, owing to the great pressure, in liquid form. Per gram of catalyst, the "Claude" process is stated to yield 6 grams of ammonia against 0.5 produced by the "Haber" process.

The nitrogen-hydrogen synthetic process for ammonia :



is largely displaced by changes in temperature and pressure (Le Chatelier's law and van 't Hoff's law) as the following table illustrates :

Temperature at °C.	Volume Percentage of Ammonia		
	Pressure, Atmospheres		
	1	100	600
400	0.38	25.1	65
500	0.13	10.6	42
600	0.05	4.2	23
700	0.02	2.2	13

Low temperature and high pressure are required for high yield, and thus the need for an effective catalyst since the natural rate of reaction decreases notably with lowering of temperature.

*References:* A survey of the world's nitrogen position is given in the annual reports of the British Sulphate of Ammonia Federation, Ltd.; *Fixation of Atmospheric Nitrogen*, by J. Knox (Gurney and Jackson, London); *Atmospheric Nitrogen Industry*, by Bruno Waeser, translated by E. Fyleman (J. and A. Churchill, London); *Fixation of Atmospheric Nitrogen*, by F. A. Ernst (D. Van Nostrand Co., New York) *The Significance of Nitrogen*, by J. E. Zanetti (Chemical Foundation, Inc., New York.)

**NITROGEN TRICHLORIDE** — See Nitrogen Compounds.

**NITROGENOUS** — Substances containing nitrogen as an important constituent, such as urea, proteins, etc.

**NITROGLYCERINE (Glyceryl trinitrate)** — See Explosives.

**NITROGLYCOL (Glycol dinitrate)** — See Explosives.

**NITRO-GROUP** — The univalent group—NO<sub>2</sub>, as present in nitrobenzene (C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>), for example.

**NITRO-HYDROCHLORIC ACID** — See Aqua Regia.

**NITRO-LIME** or "**NITROLIM**" — See Cyanamide.

**NITROMETER** — A eudiometer for measuring nitrogen gas evolved from such chemical interactions as occur between nitrates and sulphuric acid in the presence of mercury, and between ammonium salts and an alkaline solution of sodium hypobromite.

**NITRONAPHTHALENE** — See Naphthalene.

**NITROPARAFFINS AND DERIVATIVES** (Commercial Solvents Corp.) —

Four nitroparaaffins, namely, nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane, have been produced since 1940. They are manufactured by vapour phase nitration of propane and nitric acid; and are used as raw materials for syntheses and as solvents for such difficultly soluble materials as vinyl co-polymers, and cellulose acetate.

The nitroparaaffins as solvents are attractive because they are liquids of medium boiling points, mild in odour, and with strong solvent power for a wide variety of substances, including many of the new coating materials, waxes, resins, gums, dyes, and numerous organic chemicals. When blended with alcohols, the nitroparaaffins are powerful solvents for cellulose acetate and exhibit high tolerances for diluents. Their evaporation rates are approximately that of butyl acetate; they have favorable viscosity characteristics; and they are non-hygroscopic.

Since nitromethane is miscible with aromatic hydrocarbons and immiscible with aliphatic hydrocarbons, it can be used as a selective solvent for separating mixtures of these two types of hydrocarbons. Nitromethane is a component of special fuels, and a monopropellant for rockets.

Five **nitrohydroxy** (nitro-alcohol) derivatives are made by condensation of nitroparaaffins with formaldehyde. These compounds react with

TABLE SHOWING THE PROPERTIES OF NITROPARAFFINS AND THEIR DERIVATIVES

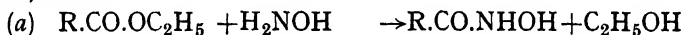
Product	Formula	Melting Point, °C.	Boiling Point °C. 760 mm. Hg	Sp. Gr. 20/20° C.	Solubility in Water, 20° C.
Nitromethane ..	$\text{CH}_3\text{NO}_2$	-29	101.2	1.139	9.5 ml. per 100 ml.
Nitroethane ..	$\text{C}_2\text{H}_5\text{NO}_2$	-90	114.0	1.052	4.5 ml. per 100 ml.
1-Nitropropane ..	$\text{C}_3\text{H}_7\text{NO}_2$	-108	131.6	1.003	1.4 ml. per 100 ml.
2-Nitropropane ..	$(\text{CH}_3)_2\text{CHNO}_2$	-93	120.3	0.992	1.7 ml. per 100 ml.
2-Nitro-1-butanol ..	$\text{C}_2\text{H}_5\text{CHNO}_2\text{CH}_2\text{OH}$	-47	105.0	1.140	20 g. per 100 ml.
2-Nitro-2-methyl-1-propanol ..	$(\text{CH}_3)_2\text{C}(\text{NO}_2)\text{CH}_2\text{OH}$	90	95.0	—	350 g. per 100 ml.
2-Nitro-2-methyl-1, 3-propanediol ..	$\text{CH}_2\text{OH}.\text{C}(\text{NO}_2)(\text{CH}_3).\text{CH}_2\text{OH}$	148	Decomp.	—	80 g. per 100 ml.
2-Nitro-2-ethyl-1, 3-propanediol ..	$\text{CH}_2\text{OH}.\text{C}(\text{NO}_2)(\text{C}_2\text{H}_5).\text{CH}_2\text{OH}$	56	"	—	400 g. per 100 ml.
Tris(hydroxymethyl)nitromethane ..	$(\text{CH}_2\text{OH})_3\text{CNO}_2$	165	"	—	220 g. per 100 ml.
2-Amino-1-butanol ..	$\text{C}_2\text{H}_5\text{CH}(\text{NH}_2)\text{CH}_2\text{OH}$	-2	178.0	0.944	Miscible
2-Amino-2-methyl-1-propanol ..	$(\text{CH}_3)_2\text{C}(\text{NH}_2)\text{CH}_2\text{OH}$	30	165.0	0.934	"
2-Amino-2-methyl-1, 3-propanediol ..	$\text{CH}_2\text{OH}.\text{C}(\text{NH}_2)(\text{CH}_3).\text{CH}_2\text{OH}$	110	151 (10 mm)	—	Miscible
2-Amino-2-ethyl-1, 3-propanediol ..	$\text{CH}_2\text{OH}.\text{C}(\text{NH}_2)(\text{C}_2\text{H}_5).\text{CH}_2\text{OH}$	38	152 (10 mm)	1.099	80 g. per 100 ml.
Tris(hydroxymethyl)aminomethane ..	$(\text{CH}_2\text{OH})_3\text{CNH}_2$	171	219 (10 mm)	—	390 g. per 100 ml.
Hydroxylammonium acid sulphate..	$\text{NH}_2\text{OH}.\text{H}_2\text{SO}_4$	Indefinite	Decomp.	—	64 g. per 100 ml.
Hydroxylammonium sulphate ..	$(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$	162	"	—	94 g. per 100 ml.
Hydroxylammonium chloride ..	$\text{NH}_2\text{OH}.\text{HCl}$	152	"	—	

organic and inorganic acids or anhydrides to form esters. Nitroölefins are formed by treatment of the esters with sodium carbonate. Amino-dioxanes can be made by condensation of a nitrodiol and an aldehyde, and subsequent reduction of the products, and xanthates by condensation of nitrohydroxy compounds and carbon disulphide in the presence of a metallic hydroxide.

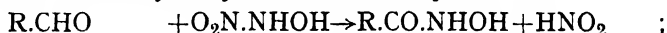
**Aminohydroxy** (amino-alcohol) derivatives are made by reduction of the corresponding nitrohydroxy (nitro-alcohol) compounds, and are among the most important derivatives of the nitroparaffins. With fatty acids, the aminohydroxy compounds form soaps that are excellent emulsifying agents. Aminohydroxy compounds are used for the synthesis of surface-active agents, pharmaceutical preparations, resins, dyestuffs, and textile chemicals. They are reactive with esters, anhydrides, and acid halides to form substituted amides; and with aldehydes, ketones, alkyl halides, and carbon disulphide.

**Hydroxylammonium salts** are derived from the nitroparaffins by reaction with concentrated inorganic acids, thus :  $R.CH_2.NO_2 + H_2SO_4 + H_2O \rightarrow R.COOH + H_2NOH.H_2SO_4$  (hydroxylammonium acid sulphate), and are used in the synthesis of pharmaceutical preparations, dyestuffs, and other organic chemicals. Aldoximes (or ketoximes) are commonly formed by reactions of aldehydes (or ketones) with hydroxylamine; and the corresponding amines from these oximes by reduction.

**Hydroxamic acids** can be prepared (1) by reaction of hydroxylamine and (a) carboxylic acid esters, (b) acid amides, (c) acid anhydrides, (d) acid chlorides, thus :

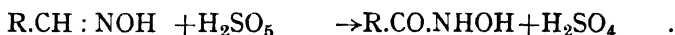


(2) by reaction of nitrohydroxylamine and aldehydes, thus :



and this reaction can be used for the detection of aldehydes by the formation with ferric chloride solution of a deep red colouration;

(3) by reaction of aldoximes with peroxymonosulphuric acid (Caro's acid) thus :



The names, formulac, and principal physical properties of the nitroparaffins and some of their derivatives have been assembled in the accompanying table.

*References* : *The Nitroparaffins*, by H. B. Hass and Elizabeth F. Riley (*Chem. Rev.*, **32**, 373-430 (1943)) ; *Nitroparaffins as Solvents in the Coating Industry*, by C. Bogin and H. L. Wampner (*Ind. Eng. Chem.*, **34**, 1091 (1942)) ; *The Nitroparaffins*, by C. L. Gabriel (*Ind. Eng. Chem.*, **32**, 887 (1940)) ; *Chem. Ind.*, Dec. 1939).

**NITROPHENOL** (*ortho*-, *meta*-, and *para*-Compounds) ( $C_6H_4(OH)(NO_2)$ ) —

Crystalline substances soluble in alcohol and ether, the *meta*- compound being used for manufacturing the dyes known as rhodamines (which are closely allied to fluorescein), whilst the *para*- compound is used in making phenacetin, and for the antiseptic treatment of raw

rubber, etc. The *ortho*- and *para*- compounds result from mixing phenol with cold dilute nitric acid, the *ortho*- compound being obtained from the mixture by distillation. The *meta*- compound is obtained by diazotizing *meta*-nitraniline, and the *para*- compound by diazotizing sulphanilic acid and treatment of the diazo compound with warm dilute nitric acid. The *ortho*- compound is yellow, and melts at 45° C. ; the *meta*- compound is also yellow and melts at 96° C. whilst the *para*- compound is colourless, and melts at 114° C. (For Trinitrophenol see Explosives (Picric Acid).)

“ **NITROPHOSKA** ” — A German make of fertilizer resembling in certain respects another product known as “ Leunaphoska,” prepared in several grades for different soils, containing nitrogen, water-soluble phosphoric acid, and potash. It has been described as essentially a ternary mixture of potassium nitrate, ammonium chloride, and ammonium phosphate, made by adding potassium sulphate or chloride containing over 50 per cent.  $K_2O$  and diammonium phosphate or dicalcium phosphate to fused ammonium nitrate. The nitrogen in both No. 1 and No. 2 qualities of “ nitrophoska ” is reported to be as one-third of the total content in the form of nitrate-nitrogen combined with potash, and the other two-thirds in the form of ammonia-nitrogen combined with phosphoric acid. The No. 2 contains more potash, and is recommended specially for light sandy soils.

**NITROSAMINES** — A series of yellow, aromatic, volatile bodies derived from the secondary bases (amines) containing the imino group :  $NH$ , by treatment with nitrous acid, such as dimethylnitrosamine,  $(CH_3)_2N.NO$ . (See Hydrazine.)

**NITROBENZENE** ( $C_6H_5.NO$ ) is an aromatic, colourless compound, m.p. 68° C., with an odour resembling that of cyanic acid, produced by interaction between nitrosyl chloride ( $NOCl$ ) and mercury diphenyl in benzene solution ; or by oxidation of diazobenzene with alkaline permanganate, or, alternatively, that of phenylhydroxylamine by means of chromic acid or ferric chloride. It yields aniline by reduction and nitrobenzene by oxidation.

**NITROSO COMPOUNDS** contain the nitroso group —  $NO$ , for example, nitrosobenzene ( $C_6H_5.NO$ ). The process of introduction of the group is styled *nitrosation*.

**NITRO-STARCH** — A nitrated preparation, made by nitrating starches with a mixture of sulphuric and nitric acids, and used in making safety explosives.

**NITROSYL** — The monovalent radical —  $N : O$  as it exists in a number of compounds, such as nitrosyl chloride ( $NOCl$ ), an orange-coloured gas resulting from the direct combination of nitric oxide with chlorine.

**NITROTOLUENE** (Nitro-Toluol) ( $CH_3.C_6H_4.NO_2$ ) — Produced by the nitration of toluene. The *para*- compound is a solid, crystalline yellow body which melts at 51° C., boils at 238° C., and is employed for

making fuchsine and other dyes in common with the *ortho*- compound, which is a yellow liquid substance which boils at 223° C., and can be used in common with nitrobenzene in preparing so-called "oil of mirbane." The *meta*- compound is yellow and crystalline (m.p. 15.5° C.). All are heavier than water, and insoluble in it, but are soluble in alcohol and ether. (For Trinitrotoluene see Explosives.)

**NITROUS ACID** — See Nitrogen Compounds.

**NITROUS ETHER (Ethyl Nitrite or Sweet Spirit of Nitre)** ( $C_2H_5ONO$ ) —

The ester of nitrous acid; a yellowish, aromatic, volatile, and inflammable liquid of sp. gr. 0.900 and b.p. 17° C.; soluble in alcohol and ether. The alcoholic solution, containing between 1.25 and 2.5 per cent. of ethyl nitrite together with acetaldehyde and other related substances, is prepared by distilling a mixture of alcohol, copper, and sulphuric acid, and is used in medicine as a stimulant and diuretic.

**NITROUS OXIDE (Laughing Gas)** — See Nitrogen (Oxides).

**NITROXAN** — A catalyst for the direct oxidation of ammonia to nitric acid by air, compounded of meta-plumbate and manganese dioxide in equi-molecular proportions, heated together in air. The nitric acid is retained as barium nitrate in the catalyst mass.

**NITROXYL** — The monovalent radical  $-NO_2$  as it exists in compounds such as the colourless gas, nitroxyl fluoride ( $NO_2F$ ), and copper nitroxyl ( $Cu(NO_2)_2$ ).

**NOMENCLATURE** — The terms and names used to identify and classify chemical substances.

Certain rules adopted by the Nomenclature Committee of the Chemical Society of London and of the American Chemical Society are as follows:

1. In naming a compound so as to indicate that oxygen is replaced by sulphur, the prefix *thio* and not *sulpho* should be used (sulpho denotes the group  $SO_3H$ ); thus,  $HCNS$ , *thiocyanic acid*;  $H_3AsS_4$ , *thioarsenic acid*;  $Na_2S_2O_3$ , sodium *thiosulphate*;  $CS(NH_2)_2$ , *thiourea*. The only use of *thio* as a name for sulphur replacing hydrogen is in cases in which the sulphur serves as a link in compounds not suitably named as mercapto derivatives; thus,  $H_2NC_6H_4SC_6H_4NH_2$ , *thio-bisaniline*. *Hyposulphurous acid*, not hydrosulphurous acid, should be used to designate  $H_2S_2O_4$ .

2. The word *hydroxide* should be used for a compound with OH and *hydrate* for a compound with  $H_2O$ . Thus, barium hydroxide,  $Ba(OH)_2$ , chlorine hydrate,  $Cl_2 \cdot 10H_2O$ .

3. Salts of chloroplatinic acid are *chloroplatinates* (not *platinichlorides*). Similarly salts of chloroauric acid are to be called *chloroaurates*.

4. Hydroxyl derivatives of hydrocarbons are to be given names ending in *-ol*, as *glycerol*, *resorcinol*, *pinacol* (not *pinacone*), *mannitol* (not *mannite*), *pyrocatechol* (not *pyrocatechin*).

5. The names of the groups  $NH_2$ ,  $NHR$ ,  $NR_2$ ,  $NH$ , or  $NR$  should end in *-ido* only when they are substituents in an acid group, otherwise

in *-ino* ; thus, MeC ( : NH)OEt, ethyl imidoacetate ;  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ ,  $\beta$ -aminopropionic acid (not *amidopropionic acid*) ;  $\text{NHPhCH}_2\text{CH}_2\text{CO}_2\text{H}$ ,  $\beta$ -anilinopropionic acid ;  $\text{CH}_3\text{C}(\text{:NH})\text{CO}_2\text{H}$ ,  $\alpha$ -iminopropionic acid.

6. Hydroxy-, not oxy-, should be used in designating the hydroxyl group ; as *hydroxyacetic acid*,  $\text{CH}_2(\text{OH})\text{CO}_2\text{H}$ , not *oxyacetic acid*. *Keto-* is to be preferred to *oxy-* to designate oxygen in the group  $\text{—CO—}$ .

7. The term *ether* is to be used in the usual modern acceptance only, and not as an equivalent of *ester*.

8. Salts of organic bases with hydrochloric acid should be called *hydrochlorides* (not hydrochlorates nor chlorhydrates). Similarly hydrobromide and hydriodide should be used. (See also *Definitive Report of the Commission on the Reform of the Nomenclature of Organic Chemistry* adopted by the International Union of Chemistry, Liège, 1930, a translation of which appears in *J. Amer. Chem. Soc.*, **55**, 3905 (1933), and in *Van Nostrand's Scientific Encyclopedia* (D. Van Nostrand Co., New York), pp. 299–302 ; "The Pronunciation of Chemical Words," a Report of the Nomenclature, Spelling, and Pronunciation Committee of the American Chemical Society (*Ind. Eng. Chem., News Ed.*, May 20, 1934, pp. 202–205 ; *Science*, Mar. 4, 1938, p. 215 ; 1948 *Report of the American Chemical Society's Committee on Nomenclature, Spelling, and Pronunciation ; The Naming and Indexing of Chemical Compounds* (*Chem. Abst.*, **39**, 5867–5975 (1945)), obtainable as a separate booklet from *Chemical Abstracts*, Columbus, Ohio, U.S.A.) ; Atoms, Chemical Compounds, Chemical Interactions, Elements, Formulas, and Rings.)

**NOMOGRAMS, NOMOGRAPHS, or ALIGNMENT CHARTS** — Charts enabling equations to be solved without calculation, by the laying of a straight-edge across several scales. Every equation requires a separate chart. Empirical relations may be similarly represented even though the equation is not known. For recording the relation between three or more variables a nomogram is more compact than a family of graphs, and is free from errors of interpolation ; but it does not give so clear a picture of the mechanism of a process. Hence nomograms are more used by engineers than by scientists. A great many have been printed in technical journals, but they generally need to be enlarged for practical use.

*References* : *Traité de Nomographie* (the classical work), by M. d'Ocagne Gauthier-Villars, Paris ; *Alignment Charts for Engineers and Students*, by Kerton and Wood (Griffin, London) ; *Chemical Engineering Nomographs*, by D. S. Davis (McGraw-Hill Book Co., New York) ; *Elements of Nomography*, by R. D. Douglass and D. P. Adams (McGraw-Hill Book Co., New York).

**NON-FERROUS METALLURGY** — See Process Metallurgy, Physical Metallurgy, Ores, and the individual metals.

**NONYLENE** — See Hydrocarbons.

**NORDHAUSEN ACID** — See Sulphur (Sulphuric Acid).

“**NORIT**” — A proprietary, heterogeneous, amorphous form of carbon of vegetable origin, with high decolourizing and filtration powers, containing about 10 per cent. moisture, 5 to 7 per cent. ash, and the remainder carbon, said to be almost thirty times as efficient as bonechar.

**NORMAL (STANDARD) STANDARD SOLUTIONS** — See Volumetric Analyses.

**NORMAL TEMPERATURE and PRESSURE for GASES (N.T.P. ; S.T.P.)** — 0° C. and 760 mm. of mercury.

**NORPINIC ACID** — An oxidation product of pinene, being 2,2-dimethylcyclobutane-1,3-dicarboxylic acid.

**NOVARSENOBENZENE (Novarsenobenzol)** — See Arsphenamine.

“**NOVOCAINE**” — See Procaine.

“**NOVOCRETE**” — A form of concrete made from cement and chemically treated (mineralized) sawdust, the latter replacing the usual aggregate of sand or gravel ; it is about one-half the weight of ordinary concrete, may be cut with a knife, receives nails readily, and is advocated for use as a building material, etc.

“**NOVOLAK**” — A phenol-formaldehyde resin.

**N.T.P.** — Normal temperature and pressure. (See same.)

**NUCLEAR CHEMISTRY AND RADIOACTIVITY** — This topic is discussed under five sections, as follows: 1. Nuclear Properties and Radioactivity. 2. Natural Radioactivity. 3. Artificial Radioactivity. 4. Applied Nuclear Chemistry. 5. Atomic Energy.

1. **Nuclear Properties and Radioactivity.** *Nuclear Structure.* The atomic nucleus is composed of closely packed neutrons and protons. The radius of the nucleus is about  $10^{-12}$  cm.—compared with the radius of the atom which is about  $10^{-8}$  cm. The number of protons in the nucleus determines the positive charge,  $Z$ , or the *atomic number* of the atom, since this charge in turn determines the number of electrons bound in the atom. Each proton and neutron has a mass very close to unity and the sum of the protons and neutrons is the mass number,  $A$ , of the nucleus. For example, sodium with 11 protons and 12 neutrons has an atomic number 11 and a mass number 23. Very often an element defined by a certain atomic number possesses two or more forms, differing only in the number of neutrons. Different atomic species of this kind are called *isotopes*. Ordinary chlorine, of atomic number 17, comprises two isotopes of mass numbers 35 and 37 in relative proportions of 76 per cent. and 24 per cent. respectively. Therefore, one isotope of chlorine has 18 neutrons, while the heavier one has 20. These isotopes of chlorine are indicated by the symbols  $\text{Cl}^{35}$  and  $\text{Cl}^{37}$ . The chemical properties of isotopes are so nearly alike that they are not separated appreciably in chemical reactions. Accordingly, chlorine wherever found has essentially the same isotopic composition. Although an element like sodium has but a single stable isotope, tin has 10 different forms and xenon 9.

Neutrons and protons are bound within the nucleus with considerable energy. The binding force is best described as a saturation force,

only effective between neighbouring particles but roughly the same between like and unlike particles. The unit of energy in nuclear measurements is the *electron volt*, *ev*, or more commonly, a larger unit, one million electron volts, *Mev*. The electron volt is the energy acquired by an electron in being accelerated across a potential difference of one volt and is equivalent to  $1.6 \times 10^{-12}$  erg. Since a nuclear change of a single atom is often accompanied by an energy change of one *Mev*, one mole of such atoms undergoing nuclear reaction would involve an energy change of about  $10^{18}$  ergs or tens of millions of kilogram-calories. Nuclear fission of a uranium atom evolves about 200 *Mev* energy.

Each proton and neutron is bound in the nucleus by an average energy of about 7 *Mev*. These binding energies are so great that a nucleus is perceptibly lighter than the sum of the masses of the neutrons and protons comprising it, according to the Einstein relation of mass (*M*)-energy (*E*) equivalence, namely,  $E=MC^2$ , where *C* is the velocity of light. Often nuclear reaction energies are expressed in mass units.

Our picture of the atom is largely the result of the conception of the nucleus by Rutherford, the extension of this model by Bohr to include the extra-nuclear electrons, and the discovery of the neutron by Chadwick.

*Nuclear Stability.* Not all possible combinations of neutrons and protons are compatible with nuclear stability. In increasing from the lowest to the highest elements, there is first a tendency for the neutrons and protons to be equal in number, but gradually more and more neutrons are required for stability. Thus the stable isotope,  $O^{16}$ , is made up of 8 neutrons and 8 protons, while stable  $Pb^{208}$  contains 82 protons and 126 neutrons. For each element there is a limited number of stable isotopes. The methods of mass spectroscopy by which the stable isotopes are identified and their relative abundances measured are due to the pioneer work of Aston in England and later work by Dempster in the United States.

If a nucleus contains too many neutrons for stability it tends to decay by negative beta-particle or *electron* emission. The negative beta-particle is an electron of nuclear origin. Beta decay may be thought of as resulting in the change of a neutron into a proton within the nucleus. In so doing the product nucleus becomes one higher in atomic number. For nuclei which are deficient in neutrons as compared to protons, the opposite change takes place—that is, the emission of a positive beta-particle or *positron*. In the case of positron emission there is a peculiar energy requirement in that approximately one *Mev* is required for the creation of the positron and its balancing electron. In many cases of radioactive decay, especially where this amount of energy is not available, an alternate process involving the capture by the nucleus of an extra-nuclear electron can take place; this process is often termed K-electron or more generally *orbital electron capture*.

Both negatron and positron decay processes are often accompanied by the emission of electromagnetic radiation termed *gamma-rays*.

Gamma-rays are emitted when the product nucleus is found in an excited state and drops to its ground state by this form of radiation. There are some cases known in which this process is not instantaneous, so that a nuclear species may exist which decays primarily by gamma-ray emission.

Among the very heaviest elements, that is, those above lead, another type of nuclear instability is noted. As the positive charge of the nucleus increases there follows a greater and greater repulsion which finally results in the emission of a positively charged particle, the *alpha-particle*. This particle has been shown to be the nucleus of the helium atom of mass number 4. The emission of an alpha-particle results in a product nucleus four units lower in mass number and two units lower in atomic number. Thus the alpha active isotope  $\text{U}^{238}$  of atomic number 92 upon decay gives the product nucleus  $\text{Th}^{234}$  of atomic number 90.

*Measurement of Radioactivity.* It may be inferred from the above that radioactivity is the manifestation of nuclear instability. In general the particles given off in radioactive decay are sufficiently energetic so that the individual particles may be measured. All energetic charged particles in traversing matter produce ionization. This ionization may then be detected by collecting the ions across a potential drop and measuring the resultant current. Common instruments for measuring radiations are the electroscope and the Geiger counter, and a large variety of highly specialized instruments have been developed. Some of these instruments will only count alpha-particles; others may be used for determining energies of beta-particles or alpha-particles.

In conjunction with ordinary counting instruments it is often possible and desirable to characterize the radiation further by filtering it through various materials such as aluminium and lead. Alpha-particles can be stopped by a very thin layer of light-weight, low-density material such as a sheet of paper. Beta-particles are considerably more penetrating, while energetic gamma-rays penetrate considerable thicknesses of heavy-weight, high-density materials, say up to one foot of concrete.

If the amount of radiation from beta-particles passing through various thicknesses of material such as aluminium is plotted against each thickness of aluminium, a characteristic absorption curve is obtained. Such absorption curves may be used in helping to identify the radiation. Absorbers are also used as filters in removing an unwanted radiation so that the remainder may be measured.

Another characteristic of radioactive decay is the rate at which the decay takes place. The number of nuclear disintegrations in unit time is proportional to the number of unstable nuclei present, therefore the decay follows an exponential law of the form  $N = N_0 e^{-\lambda t}$ , where  $N_0$  is the number originally present,  $N$  the number present at time  $t$ ,  $\lambda$  is the decay constant characteristic of the particular isotope, and  $e$  equals 2.718, the base of natural logarithms. Usually the half-life, which is equal to  $0.69/\lambda$ , is used as an index of decay rate. It is

the time in which a given radioactivity\* decays to one-half of its initial level. Half-lives are known covering a range from a small fraction of a second to tens of billions of years, but each is constant and characteristic for a given nuclear type.

**2. Natural Radioactivity.** *Reason for Occurrence.* The presence in nature of radioactive substances is a consequence of the existence of three long-lived isotopes that have survived through geological time. These are  $U^{238}$ ,  $Th^{232}$ , and  $U^{235}$ —the respective parents of the uranium, thorium, and actinium radioactive families. The shortest-lived of these,  $U^{235}$ , has a half-life of almost 1,000,000,000 years, and this is estimated as being close to the age of the earth. All three isotopes mentioned decay by a series of alpha and beta emissions, ending eventually with stable isotopes of lead. Intermediate products, of which there are some forty, have much shorter half-lives and include the familiar isotopes of radium, radon and polonium. The half-lives of these intermediate products vary from about  $10^{-7}$  seconds for  $Po^{212}$  ( $ThC'$ ) to about  $10^5$  years for  $U^{234}$ . Although these intermediate isotopes could not have survived by themselves, they are maintained through decay of their long-lived parents.

*Radioactive Families.* The uranium family, of which  $U^{238}$  is the parent, is often termed the " $4n+2$ " series, since all isotopes are divisible by the integer 4 with 2 remainder. The members of this family may be seen in the accompanying chart of the radioactive series, where ordinary uranium consists of  $U^{238}$  and  $U^{234}$  from the U-Ra series and  $U^{235}$  from the actinium or " $4n+3$ " series. The names of the members of these series, showing their genetic relations with each other, were given before the chemical elements to which they belong were known, and these historical names are shown in parenthesis.

In the chart, the sequence of decay proceeds according to the arrows. An alpha indicates alpha-decay, in which the product is lower by four units of mass and two units of atomic number. A beta-minus indicates beta-decay, in which the mass number remains the same and the product is one atomic number higher than its parent. The interval of time noted by each arrow indicates the half-life for that transition. Artificially prepared isotopes that decay into one of the natural radioactive series are shown. These are collateral branches that may have existed some time in nature but have long since disappeared because of their short half-lives (see next section).

Although the phenomenon of radioactive growth is not confined to the natural families of radioactivity, they are best illustrated here. For example, if radium is separated in pure form, only alpha activity is seen; but from this grows the rare gas radon and its gamma-emitting daughters  $Bi^{214}$  ( $RaC$ ) and others. Therefore, although radium itself is only slightly gamma-active, in a matter of a few days it produces activities\* which are intensely gamma-active.

\* Workers and writers in the field of nuclear chemistry habitually use the terms "activity", "activities", "radioactivity", and "radioactivities", in the sense that they represent concrete radioactive substances. Strictly speaking these are abstract nouns.—ED.





*Missing Series and Collateral Series.* The series represented by " $4n+1$ " is not found in nature because the longest-lived members are very short-lived compared with the age of the earth. The series has, however, been prepared artificially and bears the name "neptunium series" after the longest-lived member,  $\text{Np}^{237}$ , which has a half-life of two million years. One of the members of this new artificial series is the isotope  $\text{U}^{233}$ , which is important as a fissionable isotope and which can be prepared from thorium much as  $\text{Pu}^{239}$  is prepared from  $\text{U}^{238}$ . This series is shown in the chart of the radioactive series, as are also the collateral branches of the other three series which are produced artificially. These substances may have existed in nature at one time but due to their short half-lives have long since disappeared.

*Importance of Natural Activities.* Uranium is the primary material for atomic energy through the property of one of the isotopes,  $\text{U}^{235}$ , which undergoes fission with *slow* neutrons, and because  $\text{U}^{238}$ , the more abundant isotope, can be converted to a fissionable isotope,  $\text{Pu}^{239}$ , by the capture of neutrons. Thorium, like  $\text{U}^{238}$ , can be converted to a fissionable isotope,  $\text{U}^{233}$ .

The use of radioactivity for the treatment of malignant tumours is well known. Until the advent of artificial radioactivity, natural activities like radium and radon were the sole materials which could be used for this purpose.

One interesting use to which radium has been put is that of a portable neutron source, since when radium is mixed with a light element like beryllium a considerable number of neutrons are emitted as a result of the ejection of neutrons from the beryllium by the radium alpha-particles. In the drilling of oil wells such neutron sources have been used to indicate the presence of hydrogenous matter, that is, they allow one to tell at what level an oil vein occurs.

Most important, research with the natural radioactivities led directly to the theory of nuclear structure, to the discovery of artificial radioactivity, to the development of atomic energy, and all of the practical consequences of artificial radioactivity and atomic energy.

**3. Artificial Radioactivity.** In 1934 Irène Curie and Frédéric Joliot directed alpha-particles from polonium against aluminium and found that the radioactivity of the sample persisted after removal of the alpha source and decayed exponentially like a radioactive substance. This discovery of artificial radioactivity resulted from a transmutation of stable  $\text{Al}^{27}$  into radioactive  $\text{P}^{30}$  of three minutes half-life. About the same time instruments had been developed for accelerating charged particles to high energies. With these instruments, the first of which was the voltage-multiplier circuit of Cockcroft and Walton and the most powerful of which is the cyclotron of E. O. Lawrence, many further transmutations were made that were impossible with natural sources. The discovery of the neutron by Chadwick led to the further preparation of a great number of radioactivities that could be produced by neutron capture. This work was pioneered by Fermi and his associates. The intense neutron fluxes from the later developed

chain-reacting structure have further added to the number of artificial radioactive species. As a result there are now known more than five hundred induced radioactivities and every element from atomic number 1 to 98 inclusive is represented by at least one radioactive form. The artificial radioactive isotopes known up to 1948 have been compiled by Seaborg and Perlman (*Rev. Mod. Phys.*, **20**, 585 (1948)). The preparation of weighable amounts of artificial isotopes is possible because of the tremendous intensity of neutrons available in chain-reacting structures.

*Methods of Inducing Radioactivity.* In general a stable nucleus is made radioactive (a) by adding a particle to it, (b) by removing a particle from it, or (c) by both of these processes. These may be termed *induced nuclear reactions*. In some cases the process will result in another stable isotope, so that no radioactivity is seen. Of the particles that need to be considered, only those without charge, (1) the neutron,  $n$ , and (2) the gamma-ray,  $\gamma$ , can enter the nucleus unimpeded. Positively charged particles are repelled by coulomb forces due to the charge on the nucleus, unless they have sufficient energy to overcome this force or *potential barrier*, as it is called.

If the neutron stays in the nucleus it is bound there with considerable energy, and this so-called *binding energy* is carried off by the emission of a gamma-ray. Since a neutron may enter any nucleus and remain there through an exothermic reaction, the  $(n,\gamma)$  reaction \* is the most common nuclear reaction known. In general this reaction proceeds most efficiently with neutrons of low energy, termed *slow neutrons*. A common portable neutron source consists of a mixture of radium and beryllium. The neutrons are produced through a nuclear reaction between the alpha-particles of radium and the light beryllium nucleus. A particle accelerator like the cyclotron can produce a greater number of neutrons by allowing the particle to impinge on a target such as beryllium or lithium. Staggering numbers of neutrons appear in the chain-reacting pile as a result of the fission reaction.

When a gamma-ray reacts with a nucleus it may elevate the nucleus to an excited energy state, creating a *nuclear isomer*. Usually this energy is dissipated in about  $10^{-12}$  second through the emission of another gamma-ray. Sometimes the transition is delayed, and the radioactivity accompanying the isomeric transition may be measured as any other decay process. Only high-energy gamma-rays can dislodge a particle such as a neutron or proton from the nucleus, since it must be of sufficiently high energy to overcome their binding energies. For most nuclei this amounts to about 7 Mev. Gamma-rays or X-rays of energies up to 100 Mev have been produced in the *betatron* by allowing accelerated electrons to strike a target. Still higher gamma-ray energies are anticipated in the *synchrotron*.

Neutrons may also induce radioactivity through reactions other than the  $(n,\gamma)$  reaction. Fairly common nuclear reactions with energetic neutrons include the ejection of a proton or an alpha-particle, particu-

\* Nuclear reactions are described in a shorthand manner by enclosing in parentheses the *impinging* particle and *ejected* particle, which are separated by a comma.

larly among the lower elements. These are the  $(n,p)$  and  $(n,\alpha)$  reactions, respectively. With very energetic neutrons, that is, those above 7 Mev, it is possible to remove two or more neutrons from the nucleus upon bombardment. This  $(n,2n)$  reaction occurs somewhat more readily among the heavier elements because other nuclear reactions do not compete so strongly, and the binding energies of the neutrons decrease somewhat in going to the heavier elements. A special nuclear reaction induced by neutrons is the familiar fission reaction among the very heaviest elements. This reaction, which forms the basis of atomic energy and the atomic bomb, consists of the cleavage into two nearly equal fragments of certain heavy nuclei upon the capture of a neutron. With very high-energy neutrons such as can be produced by the Berkeley 184-inch cyclotron, much more complex nuclear reactions take place than those cited.

The most common *charged particles* that are used for inducing radioactivities are: (1) protons,  $p$ ; (2) deuterons,  $d$ ; and (3) helium ions or alpha-particles,  $\alpha$  (see Stranathan, *The Particles of Modern Physics* (Blakiston Co., Philadelphia)). The most important *instrument for accelerating* these charged particles is the cyclotron, although the Van de Graaff electrostatic generator and different types of linear accelerators have been employed successfully. Very few reactions can be produced by low-energy charged particles because of the coulomb repulsion of the nucleus. This effect varies with the charge on the nucleus and on the projectile. Thus a rather low-energy proton may enter a very light nucleus, whereas an energy of 20–30 Mev is required of an alpha-particle to enter one of the heaviest nuclei.

Before a nuclear reaction can take place, it is necessary that the particle actually enter the nucleus and become amalgamated with it. One exception to this rule takes place in the case of deuteron bombardment. Here the deuteron may break into a neutron and proton while quite close to a nucleus, and the neutron enters the nucleus unimpeded by a potential barrier. This reaction, which is actually a neutron-capture reaction, is equivalent to a  $(d,p)$  reaction and takes place with relatively low-energy deuterons. Common nuclear reactions induced by charged particles of moderate energy are as follows:  $(p,n)$ ,  $(p,2n)$ ,  $(p,d)$ ,  $(p,\alpha)$ ,  $(d,n)$ ,  $(d,2n)$ ,  $(d,p)$ ,  $(d,\alpha)$ ,  $(\alpha,n)$ ,  $(\alpha,2n)$ , and fission. Using very high-energy charged particles, that is, alpha-particles up to 400 Mev, extremely complex reactions are observed in which a score or more particles are dislodged from a single nucleus.

*Preparation of Tracers.* Under "Applied Nuclear Chemistry" will be mentioned some of the many uses to which radioactive isotopes may be put as tracers to follow the course of chemical reactions and biological distribution. Although many elements have radioactive isotopes with properties suitable for use as tracers, the methods of preparation may differ. Some important radioactive tracer isotopes are shown in the accompanying table.

If an activity can be prepared by reaction with neutrons of low energy, the chain-reacting pile is by far the most powerful source for its preparation. The most common reactions employed are the  $(n,\gamma)$ ,  
24\*

( $n, p$ ), ( $n, 2n$ ), and fission reactions. The preparation of the following important isotopes serves to illustrate :

$P^{31}(n, \gamma)P^{32}$  (14.3 days half-life)

$N^{14}(n, p)C^{14}$  (5,000 years half-life)

$U^{238}(n, 2n)U^{237}$ ;  $U^{237} \xrightarrow[6.7 \text{ days}]{\beta^-} Np^{237}$  (2 million years half-life)

$U^{235}(n, \text{fission})$ . Many fission products, including  $I^{131}$  (8.0 days half-life).

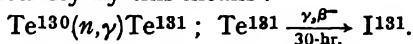
The cyclotron as a source of neutrons can also produce these reactions but at considerably lower yields. These reactions in still lower yields are obtainable through the use of a radium-beryllium mixture. The 14.3-day  $P^{32}$  can be made up to microcurie quantities with a radium source, millicurie to curie amounts can be prepared with the cyclotron, while hundreds of curies can be prepared in a pile.

TABLE SHOWING TRACER ISOTOPES OF COMMON ELEMENTS

Element	Isotope	Half-life	Method of Preparation
Carbon .. ..	$C^{14}$	5,000 years	$N^{14}(n, p)C^{14}$
Phosphorus .. ..	$P^{32}$	14.3 days	$P^{31}(n, \gamma)P^{32}$ $P^{31}(d, p)P^{32}$ $S^{32}(n, p)P^{32}$
Sulphur .. ..	$S^{35}$	87 days	$S^{34}(n, \gamma)S^{35}$ $S^{34}(d, p)S^{35}$ $Cl^{35}(n, p)S^{35}$
Calcium .. ..	$Ca^{45}$	152 days	$Ca^{44}(n, \gamma)Ca^{45}$ $Sc^{45}(n, p)Ca^{45}$
Iron .. ..	$Fe^{59}$	46 days	$Fe^{58}(n, \gamma)Fe^{59}$ $Fe^{58}(d, p)Fe^{59}$
Silver .. ..	$Ag^{110}$	225 days	$Ag^{109}(n, \gamma)Ag^{110}$
Iodine .. ..	$I^{131}$	8.0 days	$Tc^{130}(n, \gamma)Te^{131} \xrightarrow{\gamma, \beta^-} I^{131}$ Fission of $U^{235}$

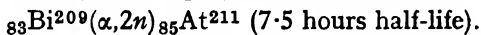
In preparing a radioisotope for use as a tracer, the *specific activity* is often an important consideration. Specific activity is defined as the ratio of radioactive atoms to the total number of atoms of the same element. High specific activities can, in general, be obtained only by irradiations in which the atomic number is changed, that is, the desired radioisotope is prepared by irradiating a different element. Since the ( $n, \gamma$ ) reaction does not directly change the element, preparation by neutron irradiation cannot be used. There are, however, some very important exceptions. The Szilard-Chalmers reaction effects a concentration of radioisotopes by an ( $n, \gamma$ ) reaction in those cases where the target element can be bound in a firm compound. The recoil energy from the gamma-ray emission can break the chemical bond holding the active atom, as a result of which the active atoms appear in a different chemical state and may be separated chemically from those that have not undergone nuclear reaction. For example, radioactive halogens can be prepared in this manner by the neutron irradiation of organic halides.

There are cases in which neutron irradiations do result in change of element. Among these are the radioactivities produced by the  $(n,p)$  reaction. Since this reaction can take place with low-energy neutrons in the case of elements of low atomic weight it becomes the best means of producing the important isotope  $C^{14}$  from nitrogen. Sometimes the  $(n,\gamma)$  reaction produces an unstable isotope which decays by beta-emission to the desired radioisotope. The 8-day  $I^{131}$  can be produced in high specific activity by this means :



A considerable number of radioactive isotopes can be formed as a result of neutron irradiation through the fission of uranium (see compilation of fission-products, *J. Amer. Chem. Soc.*, **68**, 2411 (1946)). These include elements covering the central portion of the periodic table from bromine to neodymium. Of special interest is the formation in fission of two elements not found in nature, element 43 (technetium) and element 61 (promethium) (see Elements).

Probably the most versatile tool for preparing radioactive isotopes is the cyclotron invented by E. O. Lawrence. This instrument can furnish neutrons in large numbers and, more important, deuterons and helium ions. Millicurie quantities of radioisotopes can be prepared in this manner, and many which are not accessible through neutron irradiation can be prepared with the cyclotron. As an example, the element 85 (astatine) can be prepared as follows :



Many hitherto unknown isotopes are being prepared by means of the high-energy cyclotron.

*Identification of Isotopes.* The identification of radioactive species involves the assignment of the mass number, the atomic number, the decay mechanism to varying degrees, and the energy of radiation. It is thus that radioactive isotopes are described. The identification of an isotope is extremely important in nuclear research because it is the most universally used method for deducing the nuclear reaction which produced the activity. As an example, the fission reaction was discovered by proving that the radioactive products from the irradiation of uranium with neutrons consist of a group of isotopes lying near the middle of the periodic table.

The atomic number of the radioactive isotope is most often assigned by chemical identification by the methods of *radio-chemistry*. These methods, described below under "Applied Nuclear Chemistry," consist of procedures in which the chemical identity is proved even though the chemical concentration is far too low to respond to ordinary chemical tests.

The mass number of an isotope may be assigned by one of a number of methods. The types of reactions which can take place under the conditions of the irradiation are often limited and the knowledge of the possible reactions is a useful guide. For example, irradiation with slow neutrons usually results in the production of an isotope one mass unit heavier than the target isotope. Similarly a deuteron of a

particular energy may be known to produce ( $d,n$ ) reaction in good yield but ( $d,2n$ ) reaction hardly at all. By means of "cross-bombardments" an activity may be prepared by several independent methods as a result of which a unique solution to the isotopic assignment is possible.

In some cases the unknown radioactivity is a member of a decay chain some one or more of whose members are known from independent measurements. The 12-day barium formed in fission is known to be at mass number 140 because it is the parent of 40-hour  $\text{La}^{140}$  assigned on the basis of its production from stable  $\text{La}^{139}$  by neutron capture. Many of the natural radioactivities are members of long decay chains (see previous chart) and their mass assignments were made after the genetic relationships were established.

A direct measurement of the mass number of a radioactive substance is made by means of an outgrowth of the methods of mass spectrography. The invisible quantity of the radioactive material is placed on the filament source of a special mass spectrograph and the instrument then deposits the radioactive isotopes on a surface. The position is then determined by means of a counter or a photographic plate.

Along with the isotopic assignment it is important to measure the decay properties, that is, the half-lives, and the types and energies of the radiations. Usually the cataloguing of these properties precedes the isotopic assignment, and there are many cases of well characterized radioactivities for which no mass assignment has been given.

*The Missing Elements.* Those elements preceding uranium that are not found in nature have been prepared artificially. They are technetium (element 43), promethium (element 61), and astatine (element 85). Besides these "missing elements" preceding uranium, the periodic table has been extended through element 98 by the artificial preparation of neptunium (element 93), plutonium (element 94), americium (element 95), curium (element 96), berkelium (element 97), and californium (element 98) (see Elements). All isotopes of the artificial elements are radioactive but some are sufficiently long-lived and can be prepared in such quantities that they can be isolated and their chemical and physical properties measured directly. Technetium and promethium can be produced in small quantities by cyclotron bombardment and larger quantities are made in the nuclear chain-reactors since long-lived isotopes of both elements are among the fission products. Astatine isotopes are formed by the irradiation of bismuth with helium ions in the cyclotron, and one also occurs along with an isotope of the rare element francium (element 87) in the neptunium series.

Although neptunium and plutonium were discovered through cyclotron bombardment of uranium, their preparation in macro amounts is a consequence of the attainment of a nuclear chain reaction. The famous  $\text{Pu}^{239}$  is formed from the product of neutron capture by uranium and is itself a source of atomic energy and the active ingredient of one type of atomic bomb. The long-lived isotope of neptunium,  $\text{Np}^{237}$ , is formed in a side reaction and enough has been produced to allow thorough study of its chemical properties. Using plutonium from the chain reactors as target material, americium and curium were pre-

pared by means of the cyclotron. An account of the discovery and properties of the transuranium elements is given by Seaborg (*Science*, **104**, 379 (1946)), who, with his co-workers, discovered plutonium, americium, curium, berkelium and californium.

**4. Applied Nuclear Chemistry.** *Methods of Radiochemistry.* Radiochemistry is the term applied to the methods dealing with amounts of radioactive substances present in vanishingly low concentrations and the deduction of chemical properties under these conditions. The extremely sensitive analytical tool which permits the measurements is radioactivity. Such minute concentrations of radioactive species are usually referred to as "tracer" quantities.

Tracer amounts may be precipitated from solution through the use of a *carrier*. The carrier is an inactive element added to the solution which upon precipitation brings down with it the radioactive component and it may or may not be isotopic with the latter. Since it is often desirable to obtain a radioactivity free of carrier, a non-isotopic carrier is then used which can be later separated from the radioelement by the use of some distinctive chemical property. For example, radioactive phosphorus as ferric phosphate is precipitated along with ferric hydroxide; the precipitate is then dissolved in hydrochloric acid, and the iron chloride removed by extraction with ether, leaving a pure solution containing radiophosphorus of high specific activity.

There are several mechanisms by which a micro-component becomes incorporated in a precipitate and removed from solution. These range from surface adsorption to mixed crystal formation. In true coprecipitation it is not necessary that the micro-component be isomorphous with the carrier but only that it be capable of distributing throughout the crystal lattice while the crystal is growing. The most useful guides in selecting a carrier for a radioelement are: (1) the radioelement should form an insoluble compound with the precipitant, preferably more insoluble than the carrier; (2) the radioelement should be capable of depositing in the crystal lattice of the carrier precipitate, and this latter condition implies the desirability of similar ionic radii and crystal types.

Adsorption plays an important part in radiochemistry, since the concentrations of materials are so low that very small amounts of adsorbents are often sufficient for quantitative uptake. Since any micro-component that hydrolyses to an insoluble form in solution will adsorb on vessel walls or on suspended dust particles, this phenomenon must be guarded against. This has been the cause of much difficulty in working with radioactive isotopes of certain elements. Methods of adsorption, particularly with ion-exchange resins, have been of great value in separating radioactivities, and have also accomplished other very difficult separations such as those of adjacent rare-earth elements.

Radioelements distribute between immiscible solvents as do elements at higher concentrations. For example, radioiodine can be extracted into carbon tetrachloride and radioiron as ferric chloride is extractable by ether. A wide variety of radioelements may be separated in this manner either as inorganic salts or organic complexes.

Volatility behaviour is often used to identify and separate radioactivities. Polonium and the synthetic elements astatine (element 85) and technetium (element 43) are often separated from other materials by distillation. Similarly radioelements may be plated (electroplated or chemical plated) just as larger amounts of material would be handled. As an example, radiocopper may be removed by dipping a zinc foil into the solution.

*Deduction of Chemical Properties from Tracer Behaviour.* One of the most important and interesting applications of the principles of radiochemical behaviour is the deduction of the chemical properties of a substance which can only be detected through its radioactivity. While these methods are the means by which the products of nuclear reactions are most often identified, they become the only means for the initial determination of the chemical properties of the purely synthetic elements. Even some of the natural radioactive elements such as francium (element 87) and polonium (element 84) are not normally encountered in amounts that can be examined by conventional means.

Solubility properties are determined by observing the co-precipitation behaviour with a variety of carriers. In this manner the type of ion is deduced. For example, element americium (element 95) is known to be present in aqueous solution as a trivalent ion much like the rare earths, since it is carried by insoluble lanthanum compounds but is not carried by such salts as silver chloride, barium sulphate, or insoluble sulphides. Neptunium (element 93) behaves in much the same way in the presence of strong reducing agents but loses the properties of a rare earth in the presence of strong oxidizing agents. From this it is deduced that neptunium possesses at least two oxidation states and from further tests the nature of these states may be deduced. By using a series of oxidizing agents of different potentials the oxidation-reduction potential of neptunium may be bracketed. In this way it is possible to determine most of the chemical properties of radioactive substances present in otherwise undetectably low concentrations.

*Applications to Chemistry.* Some of the applications of radioactivity techniques to problems of chemistry have been outlined above, including the discovery and determination of chemical properties of the missing elements and of the trans-uranium elements. One of the most extensive uses to which tracers have been placed in chemical work is in the study of "exchange reactions." An element in one of its valence states or forms of combination is labelled by the incorporation of a radioactive tracer in the same form and equilibrated with the inactive element in another form. Upon separation of the two forms the determination of the radioactivity will indicate whether the two forms of the element were free to interchange. Such experiments can give information about the type, strength, or reactivity of chemical bonds and the mechanism of the reaction. With the use of radioactive  $C^{14}$  rapid strides are being made in determining the mechanism of organic reactions that have been previously unsolved.

The uses of radioelements as analytical aids, in the study of diffusion processes and for a variety of other purposes, are becoming common as the availability of tracers increases.

*Applications to Biochemistry and Biology* (see Kamen, *Radioactive Tracers in Biology* (Academic Press, Inc., New York, 1947)). Organic chemistry and biological chemistry are to a great extent concerned with carbon compounds. With the general availability of  $C^{14}$  for use as a tracer for carbon, scientists in the biological fields have the greatest single tool so far devised for attacking the complex reactions of life processes. The possible uses of  $C^{14}$  are myriad and only a few can be mentioned. Recently, photosynthesis, the basic reaction upon which all life depends, has been studied with  $C^{14}$  and good progress is being made in determining the primary carbon fixation products. The complex reactions of animal carbohydrate metabolism are also being studied, as well as a variety of other reactions involving carbon compounds. The many labile compounds encountered in biological systems are particularly susceptible to measurement by radioactive techniques because of the extreme sensitivity of the method.

Many tracers other than radiocarbon are of great usefulness to the biochemist. Radiophosphorus is used to study the important organic phosphate esters; radioiodine is valuable for studying the compounds associated with the thyroid gland and for certain types of thyroid disfunction therapy.

**5. Atomic Energy.** *The Nuclear Chain Reaction.* The large-scale release of atomic energy is a consequence of two nuclear properties, namely: (1) certain of the heaviest isotopes undergo fission upon capturing neutrons, and (2) in the fission process more neutrons are created, thus making possible a chain reaction.

Almost 200 Mev of energy are released in each fission reaction, which corresponds to the staggering amount of 25 million kilowatt-hours from one kilogram of fissionable isotope. Of the nuclear species that occur in nature only the rare uranium isotope  $U^{235}$  has the necessary property of undergoing fission with slow neutrons. The more abundant  $U^{238}$  captures neutrons and after two successive beta-particle emissions becomes the important isotope  $Pu^{239}$ . This synthetic isotope has the same properties as  $U^{235}$  and is therefore itself a potential source of atomic energy. The difficulty of promoting a chain reaction with natural uranium lies in the consumption of fission neutrons by  $U^{238}$ , which, along with those lost in impurities and by other mechanisms, does not allow a sufficient number of neutrons to remain for supporting the chain reaction.

It so happens that these side reactions are favoured over the fission reaction for neutrons of energy as emitted in the fission process, but the fission reaction becomes relatively more favourable if the neutrons can be reduced in energy by a moderator. A *moderator* is the material which allows the neutrons to lose energy without capturing them by a mechanism much like the successive collisions of billiard balls. Light elements that do not have affinity for capturing neutrons are the best moderators. Carbon, as graphite, and heavy water are the two

moderators that have been used. Both types of reactors can operate with natural uranium of high purity.

In using natural uranium many of the neutrons not used in promoting the chain reaction are captured by  $U^{238}$ , which finally is converted to  $Pu^{239}$ . As mentioned above, this valuable substance is susceptible to chemical separation and constitutes the active ingredient of one type of atomic bomb. It could also be used as the material for further reactors for power production. The large plant at Hanford, Washington, is operated for the production and separation of plutonium.

Thorium is also a potential source of atomic energy. Although it cannot itself sustain a nuclear chain reaction, it is converted to the fissionable isotope  $U^{233}$  when supplied with neutrons from some other source.

*Separation of Plutonium.* The separation of plutonium after it is formed in the nuclear reactors is a large-scale complex chemical process. Plutonium occurs in minute concentration in the uranium along with prodigious levels of radioactivity from the fission products. The difficulty of the process is inherent in the necessity of separating it from many different elements where only parts per million of the initial radioactivity remain. The process must, on account of high radioactivity, be operated entirely by remote control. The principle of the process consists of repeated precipitation of carrier substances with the plutonium alternately in a reduced and oxidized condition. In one part of the cycle the plutonium is "carried" from solution, leaving in the solution those fission products that are not precipitable. Those fission products which "carry" are then removed by precipitation after the plutonium has been changed to an oxidation state that is not precipitable. A succession of such oxidation-reduction cycles serves to separate the plutonium completely from the fission products.

*Atomic Energy and By-Products.* Although the objectives of the nuclear chain reactors are to furnish plutonium and to serve as research tools, work is in progress on the design of units that will be primarily sources of power. It has been predicted that in about a generation a large part of the power used in the world may come from atomic power plants.

By-products of the nuclear chain reaction are manifold. To the research worker the new and interesting elements and radioactive tracers are of profound importance. Several radioactive elements are being used in industry.

*References:* G. T. Seaborg, "Artificial Radioactivity" (*Chemical Reviews*, **27**, 199 (1940)), which includes some 500 references to the original literature; G. T. Seaborg, "Table of Isotopes" (*Reviews of Modern Physics*, **16**, 1-32 (1944)), which includes some 600 references to the original literature; G. T. Seaborg, "The Transuranium Elements" (*Science*, **104**, 379 (Oct. 25, 1946)); G. T. Seaborg, "The Chemical and Radioactive Properties of the Heavy Elements" (*Chemical and Engineering News*, **23**, 2190 (1945)); H. Hevesy and F. A. Paneth, *A Manual of Radioactivity* (Oxford University Press, 1938); E. Pollard and W. L. Davidson, Jr., *Applied Nuclear Chemistry* (1948).

(John Wiley and Sons, New York, 1942); H. D. Smyth, *Atomic Energy for Military Purposes* (Princeton University Press, 1945) John K. Robertson, *Atomic Artillery and the Atomic Bomb* (D. Van Nostrand Co., New York); S. C. Rothman, editor, *Constructive Uses of Atomic Energy* (Harper and Brothers, New York), containing 14 lectures by eminent scientists; G. T. Seaborg *et al.*, *The Transuranium Elements* (McGraw-Hill Book Co., New York); *Atomics for the Million* ("a semi-popular account"), by M. L. Edinoff and G. Ruchlis (McGraw-Hill Book Co., New York); *Principles of Nuclear Chemistry*, by R. R. Williams, Jr. (D. Van Nostrand Co., New York); *Nuclear Fission and Atomic Energy*, by W. E. Stephens, editor (Science Press, Lancaster, Pa.); *Radioactivity and Nuclear Physics*, by James M. Cork (D. Van Nostrand Co., New York); *Nuclear Physics*, by Enrico Fermi (University of Chicago Press); *Sourcebook on Atomic Energy*, by Samuel Glasstone (D. Van Nostrand Co., New York); *Economic Aspects of Atomic Power*, by S. H. Schurr and J. Marschak (Princeton University Press).

**NUCLEAR EXPLOSION** — A nuclear reaction in which the nucleus is blown apart into many small particles, for example,  $N^{14}$  bombarded by  $H^2$  yields  $4He^4$ .

**NUCLEIC ACID** — A name given to the non-albuminous fraction of the hydrolytic products of nucleins, and consisting of a purine derivative, such as adenine, linked to phosphoric acid, and also to a carbohydrate residue, *e.g.*, glucose. These three substances are the products of complete hydrolysis of the nucleic acids. (See *Nucleic Acids*, by P. A. Levene and L. W. Bass (Reinhold Publishing Corp., New York); *Nucleic Acids*, by Walter Jones (Longmans, Green and Co.).)

**NUCLEINS (Nucleoproteins)** — A group of albuminoid substances or proteins contained in many animal and vegetable tissues, such as pus cells, blood corpuscles, and yeast cells. They are insoluble in water, but soluble in alkalis, and contain phosphoric acid in combination. Upon hydrolysis they yield albumin and nucleic acid, and subsequently various bases such as adenine, hypoxanthine, etc.

**NUCLEUS** — The central part or core of the atom, which Rutherford, in 1911, recognized experimentally from "the single large scattering of alpha-particles" as making up most of the mass of the atom and as being charged with positive electricity. The nucleus contains protons (each with mass 1, charge unit positive) and neutrons (each with mass 1, charge zero). The diameter of the nucleus is estimated to be  $10^{-12}$  cm., while the effective diameter of the atom itself is  $10^{-8}$  cm. Since the electrons (equal in number and opposite in charge to the protons) occupy very little volume, the empty space in the atom is suggestive of the astronomical space in the solar system.

**"NUJOL"** — A proprietary brand of liquid paraffin.

**"NULOMOLINE"** — A proprietary article used as a substitute for cerine in respect of certain applications, being a solution of partly elemol, 1 sugar of sp. gr. 1.4.

modera **"NE"** — See Cinchocaine Hydrochloride.

**NUT GALLS** — See Gall Nuts.

**NUT OILS and NUTS** — There are many varieties, the more important being described under their several names. Palm kernels contain about 50 per cent. by weight of a white, solid fat, which, after refining, is used in making margarine and soap, and the residual cake or meal resulting from the crushing and extraction of the oil is a serviceable cattle food. Ground-nuts or earthnuts or peanuts contain from about 35 to 40 per cent. of a liquid, palatable oil, and, when freed from the husks, about 45 per cent. of the (arachis) oil. The residual cake is highly albuminous, that from the decorticated seed sometimes testing above 50 per cent., and is much relished by cattle. Hazel nuts yield 60 per cent. of a pale yellow oil, and walnut oil, from the kernel of *Juglans regia*, is a quick-drying, green oil when freshly extracted; it turns yellow on keeping, is inodorous, and used in painting. Walnuts yield as much as from 50 to 65 per cent. of this oil, which forms a soft soap when saponified with potash. "**Nut Oil**" (**Arachis Oil**) should not be confounded with true walnut oil, which was wont to be described as "nut oil."

The approximate composition of some oily nuts, on a water-free basis, is given in the accompanying table.

Oily Nut	Fat, %	Protein, %	Starch, %
Pili .. .. .	75	13	8
Pecan .. .. .	74	11	11
Brazil .. .. .	68	18	6
Queensland .. .. .	68	9	16
Coconut .. .. .	65	8	16
Walnut .. .. .	65	17	17
Butternut .. .. .	64	29	4
Almond .. .. .	58	22	15
Pistachio .. .. .	56	23	17
Apricot .. .. .	56	33	12
Oil palm .. .. .	53	9	29
Peanut .. .. .	47	32	16
Cashew .. .. .	47	13	18

**NUTMEG** — The dried kernels of the seeds of *Myristica fragrans* (Fam. Myristicæ), a tree indigenous to the Moluccas and cultivated in Java, Sumatra, Singapore, the West Indies, and Ceylon. It is used as a condiment and for the preparation of sauces. It contains from 5 to 15 per cent. of volatile oil and about 35 per cent. of solid fat, containing myristic acid with small amounts of palmitic, oleic, linoleic, and lauric acids. (See Mace, Mace Oil, and Nutmeg Oil.)

**NUTMEG OIL (Myristica Oil)** — A colourless or pale yellow essential oil distilled from the nutmeg having a characteristic aromatic odour and taste; sp. gr. 0.880 to 0.924 at 15° C.; opt. rot. +10 to +45 at 20° C.; ref. ind. 1.472 to 1.488 at 20° C. It contains about 80 per cent. of *d*-camphene, together with *d*-pinene, dipentene, geraniol, saffrole, and myristicin (C<sub>12</sub>H<sub>14</sub>O<sub>3</sub>). It is used as a carminative and flavouring agent. (See Mace Oil.)

**NUTRITION** — See Feeding Stuffs, Foods, Hormones, and Vitamins.

**NUX VOMICA** — The dried ripe seed of *Strychnos Nux-vomica* (Fam. Loganiaceæ), a tree growing in India and the Malay Archipelago. It contains the alkaloids strychnine ( $C_{21}H_{22}O_2N_2$ ) and brucine ( $C_{23}H_{26}O_4N_2 \cdot 4H_2O$ ) which is a dimethoxy derivative of strychnine. Preparations of nux vomica are used in medicine for their bitter and stimulant properties.

**Ignatia**, consisting of the dried ripe seeds of *Strychnos Ignatii* and containing both strychnine and brucine, is sometimes used as a substitute for nux vomica ; it is grown in the Philippine Islands.

Brucine is soluble in alcohol and, when anhydrous, melts at about  $178^\circ C$ . (See Strychnine.)

**NYLON** — A completely synthetic fibre, lustrous and silky in appearance, and relatively insensitive to moisture. The elastic recovery is superior to that of natural silk, and the tensile strength is equal to or greater than that of natural or artificial silk, or synthetic rayon.

As described in U.S. Patent 2,130,948 (1938), the fibres are polyamides of protein-like structure produced from long-chain amino compounds by reaction between diamines and dibasic acids, such as the condensation of hexamethylene diamine and adipic acid, both of which may be obtained from cyclohexanol. The molten condensate is spun into threads by extrusion through orifices into an atmosphere of nitrogen. The resulting threads are then cold-drawn to about four times their original length. This increases elasticity, tensile strength, transparency, and lustre.

Nylon is especially adapted for use in hosiery, as rope, as bristles for toothbrushes, for knitted and woven goods, for transparent wrapping film, and for plastic compositions, due to its notable toughness, strength, durability, and resistance to heat and chemicals.

**o** — Ortho (see Ortho Compounds).

**OAK BARK** — The dried bark of the smaller branches and young stems of the English oak, *Quercus robur* and *Q. sessiliflora*. It contains tannin in the form of quercitannic acid, but is seldom used in medicine. (See Tannins, and Gall Nuts.)

**OAKUM** — Hemp-rope fibre, used with tar or pitch for caulking purposes.

**OBSIDIAN** — A dark green or jet variety of lava, glass-like in character, containing oxides of aluminium, magnesium, potassium, sodium, and silica ; used for making ornaments and varieties of glass. An analysis, by J. E. Whitfield, of obsidian from Yellowstone National Park (U.S.A.) is as follows :  $SiO_2$  75.52 per cent.,  $Al_2O_3$  14.11 per cent.,  $Fe_2O_3$  1.74 per cent.,  $FeO$  0.08 per cent.,  $MgO$  0.10 per cent.,  $CaO$  0.78 per cent.,  $Na_2O$  3.92 per cent.,  $K_2O$  3.63 per cent.,  $H_2O$  0.39 per cent.,  $FeS_2$  0.11 per cent.,  $TiO_2$  None,  $MnO$  None (Total 100.38 per cent.). This sample is described as a glass containing microlites of augite and ferric oxide, with traces of quartz and feldspar. (See Pumice.)

**"OBSIDIANITE"** — A proprietary brand of fire and acid proof material. (See Tower-fillings.)

**OCCCLUSION** — This term is used, chemically, in respect of the property exhibited by certain metals of adsorbing or occluding gases when exposed to them in a heated condition. Broadly, occlusion covers the retention of a gas or a liquid in or on minerals and crystals.

The behaviour of the metals platinum and palladium in this respect is referred to more particularly under those headings, and in a fine state of division, gold, iron, nickel, copper, aluminium, and lead will all adsorb more or less hydrogen gas. Iron also occludes carbon monoxide, and silver is capable of occluding oxygen gas when in a molten condition. The following data show the volumes of hydrogen absorbed by 1 volume of metal: palladium, sponge 700–800, cobalt, reduced 60–150, gold, precipitated 40–45, nickel, reduced 17–18, iron, reduced 9–19, aluminium, sheet 1–3, copper, reduced 0·5–5, silver, sheet 0·2, lead, fused 0·1. Apart from the increase in volume, there is no change in the appearance of the metals, but their density is, of course, diminished proportionately, and the combinations are regarded by some as solid solutions.

In the Faraday Lecture delivered by Theodore William Richards to the Chemical Society in 1911, it was pointed out that such porosity as occurs in rigid, compact solids usually permits the passage only of substances which enter into the chemical structure of the solids themselves. Thus, nitrogen cannot free itself from imprisonment within hot cupric oxide, although oxygen can escape; again, water cannot evaporate into even the driest of atmospheres from accidental incarceration in crystals lacking water of crystallization. Palladium, on occluding hydrogen, is obliged to expand its bulk in order to make room for even this small addition to its substance. The behaviour of platinum, nickel, and iron is probably analogous, although less marked. Fused quartz, impermeable when cold, allows of the passage of helium and hydrogen at high temperatures; but most other gases seem to be refused passage, and very many solid substances appear to act as effective barriers to the passage of hydrogen and helium, especially when cold.

For occlusion in the sense of adsorption, see Adsorption, and Colloid Chemistry.

**OCHRES** — A name given to a large number of natural pigments of clay or mixtures of clay with metallic oxides, of yellow, red, and brown colour, some of which are found naturally in a more or less pulverulent form, such as iron or red ochre, and molybdic ochre. "Yellow ochre" is a clay coloured with ferric oxide, which reddens on being burned. Some ochres contain from 20 to 25 per cent. ferric oxide ( $\text{Fe}_2\text{O}_3$ ), 50 to 60 per cent. silica ( $\text{SiO}_2$ ), and 10 to 15 per cent. alumina ( $\text{Al}_2\text{O}_3$ ), together with some water. They are used in paper-making and in the oilcloth, linoleum, paint, and varnish manufactures. (See Iron (Oxide Pigments), Umber, and Venetian Red.)

**OCTANE RATING** — The anti-knock rating of liquid fuels for internal-combustion engines is based on a test of the detonation characteristics of the fuel in a standard engine, specified by the American Society for Testing Materials (A.S.T.M.). In this test pure iso-octane (2,2,4-trimethylpentane) gives an "octane number" of 100 and normal heptane 0, and mixtures of these two hydrocarbons give intermediate values proportionally. For diesel engines a corresponding test is the cetane rating (see same).

**OCTYL ALCOHOL** — See Alcohols.

**OCTYLENE** — See Hydrocarbons.

**ODOUR** — No present theory of odour or smelling is soundly established. Practical systems of odour classification have been proposed, based on the probability that odour is registered in the brain by impressions transmitted over a limited network of nerves.

Henning proposed that odour can be represented graphically by a prism, using the six corners for six classes of odours, namely, flowery, fragrant or ethereal, resinous, spicy, burned, and putrid.

Crocker and Henderson, working with odour sensations in a search for the ultimate components, later developed a somewhat simpler scheme. As applied to the human nose, they suggest four fundamental types of odour sensation, namely, fragrance, acidity, burntness, and caprylicness. Each of these types they consider capable of being independently recognized. By a number system, the proponents claim to be able to differentiate, identify, and express some 4,000 separate sensations, although admitting that this number is insufficient to cover all known odours.

*Reference: Odors, Physiology and Control*, by C. P. McCord (McGraw-Hill Book Co., New York).

**ŒNANTHIC ACID** — See Heptoic Acid.

**ŒNANTHIC ETHER (Cognac Oil)** ( $C_9H_{18}O_2$ ) — A mobile liquid substance used in the preparation of artificial cognac and for flavouring wines; made from œnanthic acid (heptoic or heptylic acid) and ethyl alcohol by the action of sulphuric acid, and prepared commercially from the oxidized products of oil of rue. It is also described as a mixture of esters (chiefly ethyl caprate), has a strong vinous odour, and is readily soluble in alcohol and ether. Many fusel oils contain capric and caprylic acids, and some Hungarian wines are known to contain amyl caprate. Another variety of cognac oil is stated to be made by the distillation of castor oil, consisting, as is reported, of a mixture of œnanthaldehyde and undecylene. The residue left after distillation, named "floricin," is used to increase the viscosity of mineral oils, etc.

**ŒNANTHOLE** — See Heptanoic Aldehyde.

**ŒSTRADIOL (Dihydroxyœstrin, Estradiol)** ( $C_{18}H_{24}O_2$ ) — One of the female sex hormones isolated from the urine of pregnant mares in 1935 by Wintersteiner, Schwenk and Whitman. It is prepared by reduction of œstrone or from dehydroisandrosterone by Inhoffen's method (see F.I.A.T. Report No. 996 and B.I.O.S. Final Report No. 449). Œstradiol has the physiological effects of an œstrogenic hormone, causing

proliferation of the uterine endometrium and rapid growth of the epithelial tissue of the mammary gland. It is used in medicine, in the form of its monobenzoate or dipropionate, for the treatment of conditions due to deficiency of the œstrogenic hormone.

**Œstradiol Dipropionate**— A colourless, odourless, crystalline compound, obtained by reduction of œstrone and refluxing with sodium propionate and propionic anhydride followed by recrystallization from aqueous acetone; insoluble in water; sparingly soluble in alcohol; soluble in acetone and fixed oils; m.p. 103° to 105° C. In medicine it is administered as a solution in oil by injection.

**Œstradiol Monobenzoate**— A colourless, odourless, crystalline compound obtained by reduction of œstrone, benzylation and recrystallization from acetone; insoluble in water; sparingly soluble in alcohol; soluble in acetone and fixed oils; m.p. 190° to 195° C. Formerly preparations of œstradiol were standardized biologically by comparison with an international standard preparation, the basis of the test being the response obtained to administration of the hormone in spayed rats as determined by the increase in weight of the uterus. One milligram of œstradiol monobenzoate contains 10,000 units of œstrogenic activity as defined by the Health Organization of the League of Nations (international benzoate units). In medicine œstradiol monobenzoate is administered by intramuscular injection as a solution in oil.

**ŒSTRONE (Ketohydroxyœstrin, Estrone)** ( $C_{18}H_{22}O_2$ ) — A female sex hormone obtained from the urine of certain animals. It is a colourless, odourless, crystalline compound; very sparingly soluble in water; sparingly soluble in alcohol and ether; soluble in chloroform, benzene, and fixed oils; m.p. 254° to 262° C. Preparations of œstrone have been standardized biologically and 1 milligram of œstrone contains 10,000 units of œstrogenic activity as defined by the Health Organization of the League of Nations (international œstrone units). Œstrone is used in medicine for the treatment of conditions due to deficiency of œstrogenic hormone and has physiological effects similar to those of œstradiol. (See Œstradiol, and Hormones.)

**“OHMAL”** — An improved resistance alloy of the manganin type.

**OIL CAKES** — The cakes remaining after the expression or extraction of oils from seeds, used as cattle foods and fertilizers. When pressure alone is used more oil is left in the cakes than by the extraction process following upon the use of pressure, so that they are more valuable for feeding sheep and cattle. Better results are obtained when the pressure method is used by first of all heating the seed so as to coagulate the albuminous contents thus effecting better liberation of the oil.

The feeding values of cakes are chiefly represented by their protein and oil constituents. Mustard, castor oil, undecorticated cotton-seed cake, and others are chiefly used as fertilizers. (See Feeding Stuffs, and Oils.)

**OILCLOTH** — This material consists of some suitable fabric such as canvas coated with a mixture of linseed oil, whiting (or other equivalent body

material), and pigment, with or without a pattern printed on the surface. (See Linoleum.)

**" OILDAG "** — See Lubricants.

**OIL FUELS** — See Fuel (Liquid), and Petroleum.

**OIL OF VITRIOL** — See Sulphur (Sulphuric Acid).

**OILS** — There are oils of many kinds, but they may be roughly divided into three classes: (1) essential oils, which are generally described under that heading and more particularly under their individual names, and are for the most part hydrocarbons, (2) petroleum and paraffin oils, derived from natural deposits or distillation of coal, lignite, wood, peat, etc., which are also hydrocarbons, but of another class (see Petroleum), and (3) fats or fixed oils, derived from animals, vegetables, or fishes, which are obtained by pressing the nuts, seeds, or organs which contain them, by heating, or by extracting them with solvents, the more important of which are also described under their several names.

The following analyses are given by J. Van B. Gilmour.

Oil or Fat	Melting-points of Insoluble Volatile Acids Degrees C.	Melting-points of Fatty Acids Degrees C.	Melting-points of Fat Degrees C.	Iodine Values of the Insoluble Volatile Acids
Arachis .. .. .	32·1	32·0	Liquid at ordinary temperature	82·3
Cotton .. .. .	33·0	34·9	"	71·1
Sesame .. .. .	31·8	23·5	"	—
Whale .. .. .	27·2	24·0	"	—
Rape .. .. .	13·5	19·2	"	—
Palm .. .. .	46·4	44·2	37·5	—
Oleo .. .. .	40·0	41·9	35·7	—
Jus .. .. .	41·8	46·8	48·1	—
Stearine (beef) ..	43·2	48·6	53·1	—
Lard .. .. .	45·8	41·9	41·3	—
Hardened arachis ..	57·2	61·4	61·7	—
" whale (1) ..	36·0	38·2	41·2	—
" " (2) ..	37·3	42·7	44·0	—
" " (3) ..	48·2	54·5	53·5	—
Coconut .. .. .	—	—	—	1·2
Palm kernel .. ..	—	—	—	1·9

The fish oils are dealt with in another section. (See Fish Oils.)

It is on record that most vegetable and animal oils, in common with rape (colza) oil, yield petroleum oil when heated with anhydrous zinc chloride. Rape oil, by this treatment, gives a mixture of paraffins and olefins boiling at 60° to 310° C.

The fatty or fixed oils are all greasy in character, and can be made into soaps by saponification. By one process of extraction the crushed seeds are subjected to dry heat and agitation, whereby all moisture is driven off and the meal is converted into a sloppy state, and then centrifugalized at the same temperature. In this way 50 to 75 per cent. of the oil content can be extracted, so that only half of the usual pressing or other plant is required to complete the extraction.

TABLE OF CONSTANTS OF VARIOUS OILS AND FATS

Name	Sp. Gr. at 15° C.	Saponification Value	Iodine Value	Refractive Index	Melting-point Centigrade	Solidifying-point Centigrade
Almond (sweet) oil ..	0.915-0.920	190-192	93-97	1.455 at 60° C.	about -10°	-10°--21°
Arachis (nut) oil ..	0.916-0.925	185-196	85-2	1.4612 at 40° C.	about +8°	0°--±2°
Argemone oil ..	0.9220	192-7	123-7	—	—	—
Babassu-nut oil ..	—	248	15-6	—	26°	—
Bayberry (myrtle) wax	0.97-0.99	208-7	—	1.4363 at 80° C.	40°-44°	—
Beeswax ..	0.96-0.97	90-98	7.9-12.4	1.4439 at 75° C.	60 5°-64°	—
Ben oil ..	0.915	188	71	1.461	—	—
Bone fat ..	0.9009-0.9034 at 50°/30°	189.6-195.2	49.1-51.6	—	44°-45°	32.6°-33.8°
Butter ..	0.926-0.940	220-233	26-38	1.4650 at 60°	—	—
Butternut oil ..	—	199	49-5	—	—	—
Cacao butter ..	0.950-0.970	192-198	34-38	—	32°-34°	—
Candelilla wax ..	0.983-1.00	46-65	37	1.4555 at 71° C.	64°-67°	—
Candle-nut oil ..	0.925-0.927	190-214	136-140	—	18°	—
Carnauba wax ..	0.99-1.00	78-88	13	—	83°-91°	80°-81°
Cashew-nut oil ..	—	180-195	61-84	—	—	—
Castanha oil ..	0.918	193.5	106	—	0-4°	—
Castor oil ..	0.969	183-186	82-86	1.480 at 15° C.	13°	-10°--18°
Ceresine wax ..	0.92-0.94	210	96	—	74°-80°	—
Chaulmoogra oil ..	0.925	192-2	192-2	—	—	—
Chia oil ..	0.9338	80-93	1-4	—	80°-83°	—
Chinese wax (Pela) ..	0.970	190-2	140-8	—	—	—
Cockle-burr oil ..	0.9251	233-264	7-10	1.4488 at 40° C.	26°-28°	22°
Cocoonut oil ..	0.925	187-197.5	150-181	1.479-1.483 at 15° C.	21°-25°	0°-10°
Cod-liver oil ..	0.92-0.93	252	8-14	—	18°-20°	—
Coburne oil ..	0.868	196	60	—	—	—
Copal oil ..	0.917	261	14	—	—	—
Coquillo-nut oil ..	—	187.3	117-2	1.4768 at 15° C.	28°-29°	-10°--20°
Corn oil ..	0.922-0.927	193-195	103-115	1.4643 at 40° C.	35°-38°	—
Cotton-seed oil ..	0.923	188-7	121	—	—	—
Cucumber-seed oil ..	0.919	192	99	—	—	—
Curcas oil ..	0.914 at 40°	244-5	5-2	—	38-9°	—
Dika butter ..	0.92-0.93	204-7	52-5	—	—	—
Dugong oil ..	0.930	192	154	—	-26°	—
Fir-seed oil ..	0.963-0.985	77.5-83.7	21.6-28.8	—	67 3°-69.8°	—
Flax wax ..	—	227-238	—	—	55°-56°	—
Ghedda wax ..	—	—	—	—	34°-37°	—
Ghee butter ..	—	—	—	—	82°	—
Glyceria wax ..	—	—	—	—	—	—
Goat's butter ..	0.9169-0.9346 at 38°	—	24-73-34-84	1.4541-1.4559	—	—
Goose fat ..	—	192-6	72-77	—	29°-31°	—
Grape-seed oil ..	0.92-0.935	178-180	94-96.5	1.4713 at 25° C.	24°	-10°--13°
Guava-seed oil ..	0.927	197	131	—	—	—
Hazel-nut oil ..	0.9152-0.9156	190	84-85	—	—	—
Hempseed oil ..	0.925-0.928	192-193	141-148	1.448 at 15° C.	18°-19°	-27°
Henbane seed oil ..	0.921	188	136	—	—	—
Herring oil ..	0.92-0.932	180-194	120-142	1.478	—	—
Hibiscus oil ..	0.9091	189-2	89-7	—	—	—
Hongay oil ..	0.9273-0.9385	185-7	85.6-88.9	—	—	—
Hydnocarpus oil ..	0.943-0.950	191-226	—	—	20.2°-23.4°	—
Illipe-nut oil (Singapore) ..	0.9021 at 40°/4° C.	188.4	50-64	—	39°-40°	—
Irish peat wax ..	—	74	16	—	76°	—
Japanese wax ..	0.97-0.98	217-237	5-9	—	53°	—
Kapayang-seed oil ..	0.922	200-204	65-107	—	—	—
Kapok-seed oil ..	0.922-0.924	190	95	—	—	—
Kurrajong-seed oil ..	0.921	190	97	—	—	—
Lard (hog) ..	0.935	196	62	1.4539 at 60°	41-3°	—
Lard oil (cold pressed) ..	0.915-0.923	195	56-74	—	—	—
Lime-seed oil ..	0.924	197-7	109.5	1.4635 at 40°	—	—
Linseed oil ..	0.927-0.932	188-195	170-204	1.4725 at 15° C.	17°-21°	-27°
Macassar oil ..	0.86 at 99/15° C.	214.4-229.1	52.4-55	—	21°	—
Mafurra tallow ..	—	202	66	—	35°-45°	—
Maize oil ..	0.911	187-3	117-2	1.4768 at 15° C.	28°-29°	-10°--20°
Maroti oil ..	0.956	200	93-96	—	—	—
Melon-seed oil ..	0.922-0.924	190-195	115-124	1.465-1.467	—	—
Menhaden oil ..	0.927-0.933	191-196	142-180	1.480 at 15° C.	—	-4°
Mexican poppy oil ..	0.922	193	124	—	—	—

Name	Sp. Gr. at 15° C.	Saponification Value	Iodine Value	Refractive Index	Melting-point Centigrade	Solidifying point Centigrade.
Montan wax .. ..	1.00	82.8	—	—	95°-96°	—
Moura oil .. ..	0.894-0.898	190	60	—	23°-29°	—
Murumuru butter ..	0.914-0.918	240-241.5	5-12	—	34°-35°	—
Mustard oil .. ..	1.014-1.103	174	92-123	1.467-1.475 at 15.5° C.	—	—
Neat's-foot oil ..	0.914-0.918	194-199	58-70	1.469 at 20° C.	—	—
Ocuba wax .. ..	0.92	—	—	—	39.4°	—
Oiticica oil .. ..	—	188-194	145-179	—	—	—
Olive oil .. ..	0.915-0.918	185-200	74-94	1.4698 at 15° C.	24°-27°	-6° + 2°
Otoba butter .. ..	—	185	—	—	34°	—
Ozokerite wax .. ..	0.85-0.95	—	—	—	65°-80°	—
Palm oil .. ..	0.86-0.93	196-205	10.7-83.5	1.4503 at 40° C.	—	31°-39°
Palm-kernel oil ..	0.865-0.873	234-255	10.3-27.7	—	—	20°-27°
Perilla oil .. ..	0.932-0.945	189-197	193-207	1.4811 at 25° C.	—	—
Pilchard oil .. ..	0.9328-0.9313	186-189.6	170.4	1.4751 at 40° C.	—	—
Pili-nut oil .. ..	0.9069 at 30°/4°	197.4	172.7	—	—	—
Poppy-seed oil ..	0.925-0.926	193-195	133-143	1.457 at 60° C.	-18°	-18°
Porpoise oil .. ..	0.926	195-256	88-119	1.468	—	-16°
Punna oil .. ..	—	187	102	—	—	—
Rape-seed oil .. ..	0.913-0.917	170-179	94-104	1.472-1.475	17°-22°	-2°-10°
Raphia wax .. ..	0.834	51	7.7-10.7	—	82.5°	—
Rice oil .. ..	—	185	100.	1.469 at 25° C.	—	—
Rose wax .. ..	—	29.8	13	—	61°	—
Rubber-seed oil ..	0.925-0.93	185-206	117-133	—	—	—
Rye oil .. ..	0.937-0.941	173-179	118-130	—	—	—
Safflower oil .. ..	0.926	197	130-150	1.477 at 16° C.	—	—
Sakoa oil .. ..	0.917	193.5	76.6	—	—	—
Salmon oil .. ..	0.9258	182-188	161-190	1.478 at 20° C.	—	—
Sardine oil .. ..	0.93	189.0	158-190	1.4802-1.4808	28°-36°	—
Seal oil .. ..	0.924-0.926	189-196	127-193	1.474	22°-33°	-2°-3°
Sea-wolf liver oil ..	—	182-185	118-131	—	—	—
Sesame oil .. ..	0.921-0.925	188-193	103-114	1.473 at 15° C.	26°-32°	-5°
Shark oil .. ..	0.9248	188	154-172	1.476 at 25° C.	—	—
Shea butter .. ..	0.9175	179-192	56.6	—	45°	—
Soybean oil .. ..	0.920-0.926	185-195	122-135	1.4673 at 40° C.	28°	-8°
Sperm (whale) oil ..	0.871-0.880	122-144	60-93	1.46 at 25° C.	—	—
Spermaceti .. ..	0.945-0.960	122-135	3.5-6.7	—	44°-47.5°	—
Sterculia oil .. ..	0.856	191	70	—	—	—
Sterculia-kernel oil	0.868	180	62	—	—	—
Stillinga oil .. ..	0.873	200	160	—	—	—
Sugar-cane wax ..	0.961	168-177	60	—	55°-62°	—
Sunflower oil .. ..	0.924	189-193	120-136	1.461 at 60° C.	—	-16°
Taifushi oil .. ..	0.944	191	88-90	—	—	26°-29°
Tallow (beef) .. ..	0.943-0.952	193-200	38-46	1.451 at 60° C.	41.2°-52°	—
„ (mutton) .. ..	0.937-0.953	192-195	35-46	—	—	—
Tea-seed oil .. ..	0.916-0.919	194	90	1.471	—	—
Tobacco-seed oil (Dalmatian) ..	0.925	196.4	131.6	—	—	—
Tobacco-seed oil (Kentucky) ..	0.9404	196	132.8	—	—	—
Tōhaku oil .. ..	0.9329	263.8	70.8	—	—	-14.4°
Tomato-seed oil ..	0.92	191.6	114	—	—	—
Tonka-bean oil ..	0.878	198.5	72.6	1.4680 at 27° C.	7.2°	—
Tope liver oil ..	0.925	185	152	1.4803 at 15° C.	—	—
Tuna oil .. ..	—	—	156	—	—	—
Tung oil .. ..	0.936-0.943	190-195	150-176	1.503-1.518 at 20° C.	47°	-3°
Vegetable tallow (Chinese) .. ..	0.884-0.904	206	19.4-60.8	—	36°-47°	-3°
Walnut oil .. ..	0.92-0.93	192-197	142-146	1.4808 at 20° C.	—	-27.5°
Whale (Balæna) oil ..	0.908-0.925	188-196	114-126	1.465 at 40° C.	23°-29°	2°
Wool wax .. ..	0.94	102	25	1.48	35°	—

N.B.—For information as to their oil or fat contents, etc., readers are referred to the descriptions of these products in the text, and are reminded that the values given in the table are approximate only, many different figures being recorded for some of them.

**Solvent extraction** presents advantages over "pressing," and it is stated that, when properly conducted, using gasoline, for example, there is a loss of only 0.7 per cent. solvent based upon the weight of the

raw material, and still less when using trichlorethylene. In practice, the pressing and extracting processes are often combined, and the residual meals find use as cattle food. (See Extraction, and Oil Cakes.) Economic aspects of linseed, tung, perilla, soybean, and fish oils are discussed in a paper by D. H. Killeffer in *Ind. Eng. Chem.*, **29**, 1365 (1937).

The fatty or fixed oils are roughly divisible into two classes known as **drying and non-drying**. The former, such as linseed, hemp, and poppy oils, readily absorb oxygen from the air, thus forming a skin and gradually dry up, whilst the latter class (including almond, olive, and castor oils) do not so pronouncedly dry up in this way. From experiments of Eibner and Pallauf, it is inferred that the autocatalytic agent is the aldehyde peroxide primarily formed, and there are reasons for regarding the product known as linoxyn to be represented by the composition  $C_{57}H_{96}O_{20}$ . The chemistry of drying oils is further referred to under the heading of Linseed Oil.

The oxidation of drying oils is accompanied by colloidal solidification and gel formation. **Blown oils** are made from semi-drying ones, such as rape-seed, maize, and cotton-seed, by blowing air through them at from 100° to 180° C., and **boiled oils** are made from linseed and other drying oils by heating them with a small proportion of some drier, such as manganese oxide or lead oxide. The oxidation of fatty oils at ordinary temperatures and at 120° C. leads to what is known as intramolecular polymerization, and at from 200° to 300° C. the polymerization is described as bimolecular. A fish oil, blown at 230° C. for seven hours, is reported to have attained a molecular weight of 1,200 as compared with an original one of 784.

Vegetable oils undergo polymerization upon **heating**, and with the exception of linseed oil, they are said to be of low vitamin A value as compared with the chief animal oils. They have been found suitable for use as fuel in semi-Diesel engines; palm oil, cotton-seed oil, and castor oil having been tested with good results, castor oil offering special advantages, being excellent both as fuel and lubricant.

**Light**, particularly the ultra-violet rays, has an important bearing upon polymerization of fatty oils. Polymerization is most easily observed with highly unsaturated oils, such as tung and linseed oils, but it is not altogether peculiar to them. It is shown by gelatinization and by increase in density, viscosity, and mean molecular weight, together with a decrease in the iodine value.

The **refining** of edible oils by neutralization with caustic soda, deodorization and bleaching, is stated to be surpassed by a system of continuous distillation with steam *in vacuo* following bleaching, whereby the free fatty acids and odoriferous matters are removed in one operation, giving direct continuous production of a high-grade edible oil and a by-product acid oil.

For definitions of saponification, iodine, and other values of oils and fats see Fats.

*References*: "Animal and Vegetable Oils. Viscosity-Temperature Characteristics," by A. R. Rescorla and F. L. Carnahan (*Ind. Eng.*

*Chem.*, **28**, 1212 (1936)); "Swelling of Drying Oil Films in Water," by J. Rinse and W. H. G. Wiebols (*Ind. Eng. Chem.*, **29**, 1149 (1937)); reviews of "Oils, Fats, and Waxes" in *Annual Reports of the Progress of Applied Chemistry* (Society of Chemical Industry); *Allen's Commercial Organic Analysis*, vol. ii (J. and A. Churchill, London); Lewkowitsch's work on *Oils, Fats, and Waxes* (Macmillan and Co., London and New York); *The Chemistry of Drying Oils*, by R. S. Morrell and H. R. Wood (E. Benn, Ltd., London); *The Industrial Chemistry of the Fats and Waxes*, by T. P. Hilditch (Baillière, Tindall and Cox, London); *Oils, Fats and Waxes*, by Fryer and Weston (Cambridge Univ. Press); *Edible Oils and Fats*, by G. D. Elsdon (E. Benn, Ltd., London); *Vegetable Fats and Oils*, by G. S. Jamieson (Reinhold Publishing Corp., New York); Essential Oils, Fats, Fish Oils, Glycerides, Nut Oils, Oil Cakes, Petroleum, and Twitchell Process.

**OILS (Hydrogenation of)** — It has been reported that cotton-seed, linseed, ground-nut, mohua (*Bassia latifolia*), sesame, and sardine oils, after refining and hydrogenating at 180° C., using nickel catalysts, have a practically identical refractive index value at 60° C. of 1.4468. The refractive index of hardened coconut oil is much lower than that of other oils with the same iodine value. During the hydrogenation of oils an isomer of oleic acid is produced, and its presence in any quantity in edible fats is proof of the presence of hydrogenated oils; it appears to consist mainly of elaidic acid, and has an iodine value of 90. (See Oleic Acid.)

These hydrogenated products can be used in many ways, as, for example, in making chocolate fats, margarine, soaps, candles, and leather dressing. Hardened castor oil finds use as an insulating material for electrical purposes, and treated cotton-seed oil for giving a matte finish to paint compositions. (See Berginization, Coal, Hydrogenation, and Motor Spirit.)

**OITICICA OIL** — A drying oil—drying almost as fast as tung oil—used in the paint and varnish industry. Sap. no. 188–194; iodine value 145–179. The source is the seed kernels of the oiticica tree, a wild tree found in Brazil, and the seeds yield about 55 per cent. of oil.

**OLEFIANT GAS (Ethylene)** — See Hydrocarbons.

**OLEFINES (Olefins)** — See Hydrocarbons.

**OLEÏC ACID** ( $\text{CH}_3(\text{CH}_2)_7\text{CH}:\text{CH}(\text{CH}_2)_7\text{COOH}$ ) in combination with glycerine (as olein) is contained in most fats and fixed oils, particularly the latter, and when pure is a tasteless, odourless, crystalline body, of sp. gr. 0.895 and m.p. 14° C.; it is very soluble in alcohol and ether, and finds application in the textile industries and the preparation of polishing compounds. In a pure state it does not absorb oxygen from the air. Upon treatment with alkalis it yields soap.

The natural oils containing olein belong to the "non-drying" class, that is to say, they do not thicken but slowly dry up upon exposure to the air.

Oleic acid of about 93 per cent. strength, when treated with sulphuric

acid, gives rise, after the product of the first reaction is treated with water, to hydroxystearic acid, melting at  $85^{\circ}\text{C.}$ , into which product it can be almost completely converted by oxidation. J. H. Skellon has determined, among other characteristics of highly purified oleïc acid, a setting point of  $11.8^{\circ}$  to  $12.2^{\circ}\text{C.}$ , m.p.  $13^{\circ}$  to  $14^{\circ}\text{C.}$ , ref. ind. 1.4610 and i.v. 90.1.

Commercial oleïc acid is sometimes described as "Red Oil."

**Elaidic Acid** is a white, crystalline, stereoisomeric form of oleïc acid ( $\text{C}_{18}\text{H}_{34}\text{O}_2$ ), m.p.  $45^{\circ}\text{C.}$ , obtained by the action of nitrous acid upon that substance at  $200^{\circ}\text{C.}$  in the presence of sulphurous acid or sodium bisulphite.

**OLEÏN (Trioleïn)** ( $\text{C}_3\text{H}_5(\text{OOC.C}_{17}\text{H}_{33})_3$ ) — The glyceride of oleïc acid, being an oily body found present in many natural fats (particularly olive oil), and which yields stearin by hydrogenation, and oleïc acid and glycerine upon hydrolysis. Commercial oleïn should be clear above  $10^{\circ}\text{C.}$ , is easily emulsified by alkalis, free from unsaponifiable matter and neutral fat, of normal odour, and free from dirt and whale oil. (See T. P. Hilditch, *The Industrial Chemistry of the Fats and Waxes* (Baillière, Tindall and Cox, London) ; Fats, and Oils.)

**OLEINES** — See Turkey Red Oil, and Sulphonated Oils.

**OLEO** — The oil which, together with stearin, is obtained by pressing premier jus, that is, the fat expressed from beef at  $48^{\circ}\text{C.}$ , through filter-cloths. The stearin is used in making margarine, etc.

**OLEOFRACTOMETER (Jean's)** — An instrument for comparing the refractive powers of butter, fats, oils, glycerine, turpentine, etc., with standards.

**OLEOMARGARINE** — Another name for margarine.

**OLEOMETER** — A form of densimeter for taking the specific gravities of oils.

**OLEOPTENES** — See Stearoptenes.

**OLEO-RESINS** — See Balsams, and Gums and Resins.

"**OLEOSOL**" — See Lubricants.

**OLEUM** — See Sulphur (Sulphuric Acid).

**OLIBANUM (Frankincense)** — See Gums and Resins.

**OLIVE OIL** — An oil expressed from the fruit of the thornless olive-tree (*Olea Europea culta*, L., N.O. Oleaceæ), extensively grown in Spain, Italy, Greece, Turkey, and other countries of Southern Europe, Asia, and the Western States of America below latitude  $35^{\circ}$ . It is of great value as a food, and used also for the manufacture of cosmetics, pomades, "castile" and other kinds of soaps, also in respect of a great variety of commercial applications. The total world's production is estimated at about 1,000,000 tons, Spain, Italy, and Greece being the chief contributors.

Other species of *Olea* are more noted for their wood than for their oil.

The oil is mainly obtained by direct pressure of the crushed fruit, the yield being from 40 to 60 per cent., and from the pulp the remaining quantity is obtained either by steaming with hot water or by extraction with carbon disulphide or ethylene trichloride. There are a number of grades, the pure oil being of a pale yellow or greenish-yellow colour and agreeable taste; it solidifies at  $-6^{\circ}$  to  $2^{\circ}$  C., sp. gr. 0.915 to 0.918 at  $15.5^{\circ}$  C., sap. v. 188 to 197, i.v. 79 to 90, and ref. ind. 1.4605 to 1.4635 at  $40^{\circ}$  C. It contains about 84.2 per cent. of olein, 4.88 per cent. linolein, and 10.92 per cent. glycerides of saturated acids.

When carbon disulphide is used for its extraction from the pressed residue ("orujo"), which still contains from 7 to 15 per cent. oil, it is not possible to remove all traces of the solvent from the product, which is designated "sulphur olive oil," and this is used for soap-making.

"Gallipoli oil" is a crude olive oil used in the combing process of the textile trades. (See Turkey Red Oils.) The cake residue is used as a fertilizer and as fuel.

All pure virgin olive oils exhibit a yellow fluorescence under ultra-violet light. It has been ascertained that when olive oil is heated with mannitol in the presence of a small amount of sodium ethylate, the glycerol can be replaced by it, and the product is superior to the original olive oil as a food fat. (See Mannitol.)

For an account of the Spanish industry see *Ind. Chem.*, 6, 109 (1930); and of the Italian industry, *C.T.J.*, 90, 254 (1932). (See *A Textbook of Pharmacognosy*, by G. E. Trease (Baillière, Tindall and Cox, London).)

**OLIVE KERNEL OIL**, from the kernels of olives, is yellowish or green, of sp. gr. 0.918 to 0.920, sap. v. 182 to 184, and i.v. 87; soluble in ether, chloroform, and carbon disulphide, and used for soap-making, as a culinary article, lubricant, and fuel.

**OLIVENITE** — A native arsenate of copper ( $4\text{CuO} \cdot \text{As}_2\text{O}_5 \cdot \text{H}_2\text{O}$ ), of crystal system No. 4, and sp. gr. 4.13 to 4.38, found in Cornwall and elsewhere; generally green in colour, but sometimes brown or yellow.

**OLIVINE** — A group of minerals of which forsterite ( $\text{Mg}_2\text{SiO}_4$ ) and fayalite ( $\text{Fe}_2\text{SiO}_4$ ) are examples. These two minerals are seldom found by themselves but are common in isomorphous mixture. The usual mixture in which the magnesium silicate predominates is commonly known as olivine, chrysolite, or peridot. The olivine minerals are essential constituents of many eruptive rocks, such as basalt, diabase, gabbro, and peridotite. A typical alteration of peridotite rocks is into serpentine, and further into talc and clay. Canadian asbestos of commerce according to G. P. Merrill, is serpentine.

**"OLMINAL"** — Trade name for aluminium oleate.

**ONION OIL** — A yellowish liquid of penetrating odour and sp. gr. about 1.04, containing allyl compounds, including propylallyl disulphide. It is soluble in ether and chloroform, and used in flavouring.

Garlic oil contains propylallyl disulphide and allyl sulphide ( $(\text{C}_3\text{H}_5)_2\text{S}$ ), has a sp. gr. of 1.05, and is soluble in alcohol and ether.

**ONYX or CHALCEDONY** — A native coloured form of agate or nearly pure silica (a chalcedonic variety of quartz), the best specimens coming from India. (See Silica.)

**OÖLITE** — Varieties of limestone rocks, which consist of tiny concretions similar to the roe of fish.

**OPAL** — Uncleavable varieties of colloidal quartz, containing more or less water in combination. (See Silica.)

**OPIUM** — The inspissated latex obtained from the unripe capsules of *Papaver somniferum*, a species of poppy grown in Turkey, Bulgaria, Yugoslavia, Egypt, Greece, India, and China. An incision is made into the wall of the capsule and the exuded latex allowed to evaporate before collection. The partially dried latex is collected, massed together, further dried, and formed into cakes or bricks which are wrapped in poppy leaves or paper. Various commercial varieties of opium are known. Turkish opium occurs as "Soft Shipping" opium, which may contain as much as 30 per cent. of moisture, and as "Drug-gists'" opium, which is of a firmer consistency and contains about 20 per cent. of moisture. Persian opium contains less moisture than Turkish opium and is usually in the form of bricks weighing about one pound wrapped in red paper.

Opium contains a number of alkaloids, the principal constituents being morphine, codeine, papaverine, narcotine, narceine, and thebaine. The alkaloids occur partly free and partly combined with sulphuric acid and meconic acid ( $C_7H_4O_7$ ). The morphine content may vary from 5 to 21 per cent. in crude opium and the British Pharmacopœia stipulates that opium for medicinal purposes must contain not less than 9.5 per cent. of anhydrous morphine. Powdered opium is a standardized powder containing 10 per cent. of anhydrous morphine. Other substances present in opium are mucilage, carbohydrate, wax, and rubber.

By extraction with warm water and addition of an equal volume of alcohol and excess of ammonia, morphine and narcotine are precipitated and the narcotine can be extracted from the precipitate with benzene or chloroform, the morphine being insoluble. When the mother liquor is treated with acetic acid, salts of the strong bases (codeine and thebaine) are formed and the papaverine may then be extracted with benzene. The mother liquor yields thebaine by precipitation with ammonia or alkali, codeine remaining in solution.

The following are the main characteristics of the principal alkaloids :

**Morphine** ( $C_{17}H_{19}O_3N \cdot H_2O$ ), white crystalline solid, sparingly soluble in water, soluble in alcohol and ether, m.p.  $254^\circ C$ .

**Codeine** ( $C_{18}H_{21}O_3N \cdot H_2O$ ), white crystalline solid, soluble in water, alcohol, and ether, m.p.  $155^\circ C$ .

**Thebaine** ( $C_{19}H_{21}O_3N$ ), white crystalline solid, soluble in water, alcohol, and ether, m.p.  $193^\circ C$ .

**Papaverine** ( $C_{20}H_{21}O_4N$ ), white crystalline solid, insoluble in water, soluble in hot alcohol and benzene, m.p.  $147^\circ C$ .

**Narceine** ( $C_{23}H_{27}O_8N \cdot 3H_2O$ ), white crystalline solid, sparingly soluble in water, soluble in alcohol, m.p.  $170^\circ C$ .

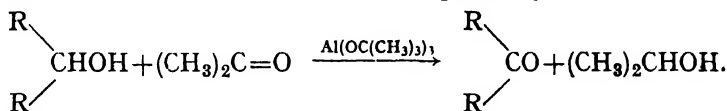
**Narcotine** ( $C_{22}H_{23}O_7N$ ), white crystalline solid, insoluble in water, slightly soluble in alcohol and ether, soluble in chloroform, m.p.  $176^\circ C$ .

Preparations of opium are used in medicine for their narcotic and analgesic properties.

*References*: Streatfield Memorial Lecture on "Opium," by J. R. Nicholls, at the Royal Institute of Chemistry, London, in 1938; H. A. Henry, *The Plant Alkaloids* (J. and A. Churchill, London).

**OPOPANAX** — See Gums and Resins.

**OPPENAUER REACTION** — This reaction consists in the oxidation of a secondary alcohol to a ketone, using a large excess of acetone in the presence of aluminium tertiary butoxide. Good yields are obtained and the oxidation is confined to the secondary alcoholic group, any unsaturated centres in the molecule being entirely unaffected.



**OPSONINS** — See Bacteria.

**OPTICAL ACTIVITY** — See Light.

**OPTOPHONE** — See Selenium.

**ORANGE OIL** — A volatile oil obtained by expression from the fresh peel of *Citrus sinensis* (oil of sweet orange) or *Citrus Aurantium* subsp. *amara* (oil of bitter orange). Chemically the two oils are very similar but are distinguishable by their odour and taste. Oil of orange contains about 90 per cent. of *d*-limonene with decyl aldehyde, methyl anthranilate, and traces of terpineol and linalol; sp. gr. at  $15^\circ C$ . 0.848 to 0.852 (sweet orange), 0.852 to 0.856 (bitter orange); opt. rot.  $+95^\circ$  to  $+99^\circ$  (sweet orange),  $+88^\circ$  to  $+96^\circ$  (bitter orange); ref. ind. at  $20^\circ C$ . 1.472 to 1.474 (sweet orange), 1.472 to 1.475 (bitter orange).

**ORANGE-FLOWER OIL** — See Neroli Oil.

**ORANGEITE** — A mineral, amorphous, hydrated silicate of thorium, of sp. gr. 1.9 to 2.3. (See Thorium.)

"**ORARSAN**" — See Acetarsol.

**ORCHIL** — See Archil.

**ORCINOL** ( $C_6H_8 \cdot (\text{CH}_3)(\text{OH})_2(1, 3)$ ) is stated to be contained in the free state in the various orders of lichens (referred to under the heading of archil), which are used for the production of litmús and archil, as also in the many acids and ethers which can be distilled from these lichens, although it is chiefly produced by the decomposition of orsellinic acid ( $C_7H_6(\text{COOH})(\text{OH})_2$ ). It is prepared by crushing 5 parts of *Rocella fusiformis* with 55 parts of calcium lactate and 2 parts of lime, filtering the mush, treatment of the filtrate with hydrochloric acid to

precipitate erythrin, and heating the product with alkali, thus forming orcinol. It is a crystalline body which can be distilled at 288° C. without decomposition, and can be rendered anhydrous by exposure over sulphuric acid. It has a sweet taste, and in contact with ammonia and air it is converted into orcein ( $C_{28}H_{24}O_7N_2$ ), assuming a deep purple colour. The anhydrous crystals of orcinol melt at 107° C. (See Archil, and Lichens.)

**ORDEAL BEAN** — See Calabar Bean.

**ORDER-DISORDER REACTIONS** — A solid solution phenomenon in which a random pattern of different atoms becomes preferentially arranged on lattice sites so that one species is systematically surrounded by atoms of other species and *vice-versa*. This atomic interchange within a phase reflects itself in the chemical, electrical, magnetic, mechanical, specific heat, and X-ray diffraction behaviours of alloys. The  $Cu_3Au$  alloy is a classical example in this respect. (For a comprehensive treatment of order-disorder transformations in alloys, see the paper by F. C. Nix and W. Shockley in *Rev. Mod. Phys.*, 10, 1 (1938).)

**ORES AND THEIR TREATMENT** — Ores are metals or compounds of metals as found in nature, derived from the outer crust of the earth, and concentrated by natural processes. Kemp defines ores as "metallic deposits and other minerals that are extracted for their economic value." An economic classification of ores frequently comprises the three divisions, namely, (1) metallic, (2) fuel, and (3) non-metallic-non-fuel.

The geologist indicates how ores can be found, and it is the function of the chemist to utilize them. Veins or *lodes* differ in character from the rock environment, while *outcrops* are mineral deposits occurring at the surface, the "gangue" is valueless vein-matter. Ore deposits are sometimes found in gravel and other alluvial deposits, and in other cases disseminated through igneous and sedimentary rocks. As a rule, only materials of a certain grade of richness can be worked profitably, but others with small percentages, such as some tin ores, containing as low as 1 per cent. of the metal, may be successfully handled—it depends upon many circumstances, such as the value of the ultimate product and the cost of production.

From a number of considerations it has been suggested that the earth consists of a vast metallic ore composed mainly of an alloy of iron and nickel enclosed in a comparatively thin shell of earthy minerals.

The generally accepted view of the formation of mineral deposits is that (1) they have been solidified from molten matter as igneous rock; (2) have been deposited mechanically by breaking up of some pre-existing rock; (3) have been produced by chemical interaction; or (4) organically from a solution derived from some older rock; and that from such changes the four classes of minerals result, namely, igneous, sedimentary, chemical, and organic.

The treatment of ores, with the view of separating their various metallic or other constituents, necessarily varies according to their nature, and many of the processes, including oxidation by roasting, etc., are described under the headings of the individual metallic

elements. (See Aluminium, Copper, Gold, Iron, Lead, Nickel, Silver, Tin, and Zinc; and Economic Aspects for Production by Countries.)

In the "cyanidation" treatment of gold and silver ores of Northern Canada, calcium cyanide is said to be supplanting potassium and sodium cyanides. Prepared as "Aero Brand," it contains some 50 per cent.  $\text{Ca}(\text{CN})_2$ , 10 per cent.  $\text{CaO}$ , and a little  $\text{NaCN}$ , and is made by fixing pure nitrogen in powdered calcium carbide at a white heat. Metallic gold and silver are dissolved as double cyanides. (See *Cyanidation and Concentration of Gold and Silver Ores*, by J. V. N. Dorr (McGraw-Hill Book Co., New York).)

For the treatment of mineral ores, fuel residues, etc., by **magnetic separation**, several types of machines are available.

A method of separation largely used, particularly in respect of lead and zinc sulphides, is that known as **flotation**, in which various liquids such as amyl alcohol, creosote oils, cresylic acid, eucalyptus oil, pine spirit, and turpentine are variously employed, while in the case of copper ores petroleum products are favoured. The powdered ore is mixed with water in the proportion of about 1 ton to 4 or 5 tons, and there is then added from  $\frac{1}{2}$  to 2 pounds of the "flotation" agent, so as to produce frothing when air is blown through the mixture, with the result that the sulphide ore concentrates in the froth, while the quartz and other impurities sink to the bottom or remain in slight suspension in the water; sometimes an oxidizing agent is also added. Alkaline xanthates are sometimes used as "absorbing collecting agents," inducing the mineral particles to cling together at the interface between the aqueous solution and the frothing agent layer.

The important factors are agitation, solubility or miscibility of the flotation liquid (usually oil), the surface tension, and the size of the ore particles, these factors being interdependent, as the more the oil goes into solution, the more the bubbles are diminished.

It would appear that the flotation process depends upon the adequate formation of flocculent aggregates of solid particles and air bubbles, independently of opposing electrical charges. Again, it is stated that the selective agency by means of which the flotation method separates substances like galena from its associated quartz and calcite depends in the main on the contact angle formed by the oiled surfaces. In other words, the mineral sulphides, etc., are wetted by certain oily bodies and not by water, which, on the other hand, gives preference to quartz in the capacity of wetting.

The froth may be broken up by spraying with water, but usually the concentrates are passed direct into a pressure filter, thus collecting the solid separated ore for such further treatment as may be expedient.

The froth-flotation process has also been applied to the purification of coal by the elimination of shale and other waste material with which it may be associated.

It is to be noted that many substances of greater density than water will float when dusted on it in a pulverized condition, particularly those which are insoluble in it, while others can be made to float or be

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involved in froth by increasing the density of the medium or attachment of oily matter to the ground material to be treated.

Ores containing as little as 0.5 per cent. copper in the form of sulphide have been successfully treated, 90 per cent. of the copper being recovered as concentrate assaying some 20 per cent. of the metal.

**Regulators** are used to control the hydrogen-ion concentration. As a mildly alkaline solution generally works best, lime is commonly used. **Activators** are used to impart a lustrous coating to the particles of minerals, as when sphalerite (zinc sulphide) is treated with a little copper sulphate, and when lead carbonate ores are treated with small amounts of sodium sulphide. **Frothers**, such as pine oil and cresylic acid, are added to make the air bubbles more permanent. **Collectors** or **promoters** influence the capacity of the air bubbles to carry the particles of minerals. Potassium ethyl xanthate and other xanthates are used for this purpose, and it is stated that as little as one ounce of certain collectors per ton of ore will increase the mineral recovery from 30 per cent. up to as much as 90 per cent. **Depressors** act on the unwanted fraction of the ore, that is, the gangue materials, to reduce the tendency to carry them into the froth. The cyanides are most commonly used, and sulphites and silicates less frequently.

For the treatment of a total of 18.7 million short tons of ore by flotation processes in a recent year the following quantities of reagents are reported, namely, 49,000,000 pounds of lime for 12,400,000 short tons of ore ; 4,500,000 pounds of copper sulphate for 4,800,000 short tons of ore ; 1,500,000 pounds of cresylic acid for 9,300,000 short tons of ore ; 1,300,000 pounds of pine oil for 12,600,000 short tons of ore ; and 1,100,000 pounds of ethyl xanthate for 8,400,000 short tons of ore.

In the froth flotation of coal, the addition of starch solution and certain other substances is stated to inhibit the flotation of fusain, which may thus be separated from the clarain and vitrain constituents of the coal. (See Coal.)

The output of minerals and principal metals of the world is shown in the entry Economic Aspects.

(See *Flotation*, by Mayer and Schranz (S. Hirzel, Leipzig) ; *Flotation*, by A. M. Gaudin (McGraw-Hill Book Co., New York) ; Calcination, Clay, Elutriation, Furnaces, Levigation, Metallography, Metallurgy, and Minerals.)

**ORGANIC ANALYSIS** — The analysis of an organic compound falls into the following parts :

(a) *Identification of the Elements present.* Carbon is, of course, always present and hydrogen almost always. The majority of compounds also contain oxygen, and a very large number contain nitrogen. Of less frequent occurrence are the halogens, sulphur, and the metals, while quite a large number of compounds contain phosphorus and arsenic. The remaining elements are not often encountered, but any of them may be present, e.g., metallic elements in salts.

(b) *Determination of the Percentage Composition.* Methods are available for the quantitative determination of all the elements, although oxygen is almost always calculated by difference. From a

knowledge of the percentage composition the empirical formula may be calculated, but the actual molecular formula can only be found by a determination of the molecular weight.

(c) *Determination of the Molecular Weight.* In the case of volatile compounds this is easily ascertained by determining the vapour density and calculation of the weight of 22.4 standard litres. For other substances other methods have to be adopted, such as the depression of the freezing point in a selected solvent.

From the above results one is able to calculate the molecular formula of an organic compound, but the structural formula can only be ascertained from a knowledge of the chemical reactions or the methods of synthesis, or both.

For the identification of organic compounds it is not generally necessary to perform all the above operations, as a knowledge of the elements present and the reactions of the compound, together with one or two physical constants, such as the melting or boiling point, is usually sufficient to enable one to make a correct deduction of the identity.

(See *Handbook of Organic Analysis*, by H. T. Clarke (E. Arnold and Co., London); *Organic Analysis*, by Barnett and Thorne (University of London Press); *A Student's Manual of Organic Chemical Analysis*, by J. F. Thorpe and M. A. Whiteley (Longmans, Green and Co., London and New York); *Laboratory Manual of Organic Chemistry*, by H. L. Fisher (John Wiley and Sons, New York); *Qualitative Organic Analysis*, by O. Kamm (John Wiley and Sons, New York); *The Systematic Identification of Organic Compounds*, by R. L. Shriner and R. C. Fuson (John Wiley and Sons, New York); *Identification of Pure Organic Compounds*, by E. H. Huntress and S. P. Mulliken (John Wiley and Sons, New York); and Allen's *Commercial Organic Analysis* (J. and A. Churchill, London).

**ORGANIC CHEMISTRY** — The study of the compounds of carbon, sometimes excluding the metallic carbonates and cyanides. Reputed to be one of the most masterly systematized fields of science. Articles and treatises in this field are many and for the most part excellently executed. Some books of study and reference are given here: *Organic Chemistry for Advanced Students*, by J. B. Cohen (E. Arnold and Co., London); *Textbook of Organic Chemistry*, by A. F. Holleman (Chapman and Hall, London); Julius Schmidt's *A Textbook of Organic Chemistry*, by H. G. Rule (Gurney and Jackson, London); *Organic Chemistry*, by F. C. Whitmore (D. Van Nostrand Co., New York); Bernthsen's *Organic Chemistry*, by Sudborough (Blackie and Son, London); *Practical Organic Chemistry*, by Sudborough and James (Blackie and Son, London); *Organic Chemistry*, by L. J. Desha (McGraw-Hill Book Co., New York); *Reactions of Organic Compounds*, by W. J. Hickenbottom (Longmans, Green and Co., London); *The Chemistry of Carbon Compounds*, by J. B. Conant (Macmillan Co., New York); *Textbook of Organic Chemistry*, by John Read (G. Bell and Sons, London); *An Introduction to Organic Chemistry*, by R. J. Williams (D. Van Nostrand Co., New York); *Fundamental Principles of Organic*

*Chemistry*, by Charles Moureu (Harcourt Brace and Co., New York) ; *Organic Chemistry*, by Louis F. and Mary Fieser (D. C. Heath and Co., Boston) ; *Textbook of Organic Chemistry*, by E. Wertheim (The Blakiston Co., Philadelphia) ; and *Organic Chemistry*, by Paul Karrer (Elsevier Publishing Co., New York).

**ORGANO-METALLIC COMPOUNDS** — Comprise a numerous class of colourless, mobile, liquid substances of volatile character in which organic radicals, such as the alkyl groups, are combined with metals ; for example, zinc dimethyl ( $\text{Zn}(\text{CH}_3)_2$ ), zinc diethyl ( $\text{Zn}(\text{C}_2\text{H}_5)_2$ ), aluminium trimethyl ( $\text{Al}(\text{CH}_3)_3$ ), and lead tetraethyl ( $\text{Pb}(\text{C}_2\text{H}_5)_4$ ). Zinc dimethyl and zinc diethyl are heavy, colourless liquids, boiling at  $46^\circ$  and  $118^\circ$  C. respectively, and spontaneously fire when exposed to the air. By oxidation, zinc diethyl yields zinc ethylate ( $\text{Zn}(\text{OC}_2\text{H}_5)_2$ ), and this by further oxidation gives zinc acetate ( $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2$ ).

Mercury, tin, and some other metals yield phenyl derivatives, mercury phenyl ( $\text{Hg}(\text{C}_6\text{H}_5)_2$ ), for example (obtained by the action of sodium amalgam on bromobenzene). Some other organo-metallic compounds are described under the respective metals concerned. (See vol. xi of J. N. Friend's *Inorganic Chemistry* (Griffin and Co., London) ; chap. xix of Morgan and Burstall's *Inorganic Chemistry: A Survey of Modern Developments* (W. Heffer and Sons, Cambridge) ; Gilman's *Organic Chemistry*, p. 489 (John Wiley and Sons, New York).)

**ORGANOSOLS** — Colloid disperse systems having organic liquids as the dispersion medium. (See Colloid Chemistry.)

**ORIENTATION** — The relative positions of substituted constituents in relation to the parent substance and each other.

**ORIGANUM OIL** — See Thyme Oil, and Thymol.

**"ORLON"** (Du Pont) — Trade-mark for fibre-forming polymeric acrylonitrile units. It possesses notably high tensile strength both dry and wet ; high stability to dry and wet cleaning ; high covering power ; low moisture absorption ; high resistance to mould and mildew ; high resistance to wrinkling ; quick setting ability ; and high resistance to deterioration by sunlight and weathering. In respect to sunlight and weather resistance it far exceeds cotton, silk, viscose, rayon, or nylon.

**ORMOLU (Mosaic Gold)** — See Alloys, and Mosaic Gold.

**ORPIMENT** — The mineral arsenic trisulphide ( $\text{As}_2\text{S}_3$ ) of crystal system No. 4, and sp. gr. 3.5. (See Arsenic Compounds.)

**"ORR'S ZINC WHITE"** — See Paints.


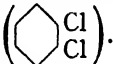
**ORRIS OIL** — A yellowish, semi-solid, fatty substance distilled from the rhizome of *Iris florentina*, *I. pallida*, and *I. germanica*, natives of the South of Europe. It melts at  $44^\circ$  to  $50^\circ$  C., is soluble in alcohol and ether, and used in making perfumes and cosmetics. It contains myristic acid (85 per cent.) and proportions of caprylic, pelargonic, capric, undecylic, lauric, tridecylic, and benzoic acids, together with irone (5 to 10 per cent.) ; has a sp. gr. of 0.93 at  $15^\circ$  C., and opt. rot.  $+12^\circ$  to  $+30^\circ$  at  $20^\circ$  C. (See Ionone, and Irone.)

**ORTHITE (Allanite)** — Crystal system No. 5, and sp. gr. 3.0 to 4.0. A published analysis of a specimen from Ambatofotiskely is as follows:  $\text{SiO}_2$  30.42,  $\text{ThO}_2$  2.37,  $\text{Al}_2\text{O}_3$  17.00,  $\text{Ce}_2\text{O}_3$  8.09,  $\text{La}_2\text{O}_3$  8.13,  $\text{Y}_2\text{O}_3$  1.42,  $\text{Fe}_2\text{O}_3$  5.45,  $\text{FeO}$  11.96,  $\text{MnO}$  0.80,  $\text{CaO}$  13.38,  $\text{H}_2\text{O}$  0.73 per cent. (See Europium, and Lanthanum.)

**ORTHOCAINE** ("Orthoform") ( $\text{C}_8\text{H}_9\text{O}_3\text{N}$ ) — A white or slightly off-white, odourless, crystalline powder, being the methyl ester of *m*-amino-*p*-hydroxybenzoic acid; sparingly soluble in water; soluble in alcohol; slightly soluble in ether; m.p.  $141^\circ$  to  $143^\circ\text{C}$ . It is used in medicine as a surface anæsthetic for mucous surfaces.

**ORTHOCLASE** — A kind of felspar or potassium aluminium silicate of crystal system No. 5, and sp. gr. 2.4 to 2.6.

**ORTHO COMPOUNDS** are substitution products derived from benzene, in which the substituting radicals or groups are constitutionally situated in certain definite *adjacent* positions on the nucleus, for example, *ortho*-

cresol () and *ortho*-dichlorobenzene (). The positions are now more commonly expressed numerically, for example, 1, 2-dichlorobenzene for the latter substance, and 2-methylphenol for the former. (See Benzene Ring.)

**ORTHO-CRESOL** — See Cresol.

**ORTHO-NITRANILINE** — See Nitranilines.

**ORTHO-TOLUIDINE** — See Toluidine.

"**ORVUS**" — See Soaps (Sulphated Alcohol).

**OSAGE ORANGE** — A material obtained from the bark of the osage orange tree (*Maclura aurantiaca*, N.O. Moraceæ), of the same genus as fustic, indigenous in North America, containing some 25 per cent. tannin, and used as a dye.

**OSAZONES** — Condensation compounds of sugars and phenylhydrazine used to separate and identify individual sugars.

Osazone of	Melting Point, $^\circ\text{C}$ .	Mulliken Time Test of Formation
Galactose .. ..	214	15-19 min.
Glucose .. ..	205	4-5 min.
Fructose .. ..	205	2 min.
Mannose .. ..	205	—
Maltose .. ..	205	—
Lactose .. ..	200	—
Arabinose .. ..	167	10 min.
Xylose .. ..	—	7 min.
Sucrose .. ..	None	—
Raffinose .. ..	None	—

**OSMIRIDIUM (Iridosmine)** — A natural deposit containing osmium and iridium, with varying proportions of rhodium, ruthenium, and platinum, found together with platinum deposits and certain gold washings. It occurs for the most part in irregular grains of sp. gr. about 20.0, and is recovered to some extent from "banket ore" of the Rand mines, and from mineral deposits near Waratah, Tasmania. When heated in the air, it is stated to give off osmium tetroxide. The "black sands" collected from the amalgamation plates, etc., are stated to contain iridium to the extent of 3 ounces per ton. (See Iridium.)

**OSMIUM (Os) and its Compounds** — Atomic weight, 190.2. See Elements for other data. A rare element of the platinum group, and the most refractory; found in alloyed association with iridium in certain platinum ores, and notably in so-called *osmiridium*, in parts of which the osmium content runs as high as from 30 to 40 per cent.

Osmium is a hard, bluish-white metal, possessing catalytic properties and the highest specific gravity of any known material. It can be prepared from its oxides by reduction; is known in crystalline and black amorphous forms, and burns brightly when strongly heated, forming osmium tetroxide, which can be condensed in crystalline white needles. The amorphous variety is dissolved by aqua regia, and the tetroxide is thus produced, but the compact form is insoluble in all acids.

Osmium forms alloys with many metals, and is used as a hardener for platinum and palladium alloys. The osmium-iridium-ruthenium alloys have been developed for special electrical parts and thermal devices. Osmium alloys have also found uses as bearings for small instruments, replacing jewels, as pivot and pen points. Its compounds find more applications than the pure metal, which is both expensive and difficult to work.

Four **oxides** are known, namely, the monoxide ( $\text{OsO}$ ), the sesquioxide ( $\text{Os}_2\text{O}_3$ ), the dioxide ( $\text{OsO}_2$ ), and the tetroxide ( $\text{OsO}_4$ ). The tetroxide (osmic acid) is used in medicine and, to some extent, in making incandescent gas mantles, in photography, in microscopy for staining, and as a reagent for adrenalin and indican.

Three **chlorides** are known, namely,  $\text{OsCl}_2$ ,  $\text{OsCl}_3$ , and  $\text{OsCl}_4$ .

There are some **salts** corresponding to the sesquioxide.

**"OSMO-KAOLIN"** — A proprietary colloidal aluminium silicate prepared by a patented electro-osmose method.

**"OSMO-SIL"** — An amorphous form of silica of great purity, prepared by the electro-osmose process, and used as a powerful absorbent for dye-stuffs, etc.

**OSMOSIS** — If a sugar solution is separated from pure water by a semi-permeable membrane, such as copper ferrocyanide deposited on porous earthenware, the water will pass through the membrane into the sugar solution. This phenomenon, called *osmosis*, was first observed and recorded by Abbé Nollet in 1748 and was studied by Pfeffer and van 't Hoff in 1877. If sufficient pressure is applied to

the sugar solution, by means of a piston or by a high column of the solution itself, the passage of the solvent into the solution will appear to cease, and if the pressure is increased still further the flow will be reversed. The pressure which must be applied to the solution to prevent the osmotic flow of solvent through the membrane into the solution is called the *osmotic pressure* of the solution.

The mechanism of osmosis probably can best be understood by citing one further illustration. Place a tall jar containing sugar solution and one containing pure water side by side under a vapour-tight bell-jar. Upon observing the experiment after several days the volume of the water will have decreased and the volume of the solution correspondingly increased. If sufficient time is allowed to elapse all of the water will disappear and an equal volume of liquid will appear in the sugar solution.

This phenomenon can be explained by the fact that the vapour pressure of water is greater than the partial pressure of water in the sugar solution. Thus, the escaping tendencies (vapour pressure) of water being greater in pure water than in the sugar solution, the water will evaporate from the pure water container and condense in the sugar solution (see Vapour Pressure). The phenomenon of osmosis is essentially the same.

Consider the membrane in an osmotic cell as being the air into which only solvent (water) molecules can diffuse. The diffusion pressure of the solvent molecules in the pure solvent will be greater than the diffusion pressure of solvent molecules in the solution (Raoult's law). Thus there will be an over-all flow of solvent molecules from the pure solvent into the solution. However, when a sufficiently large pressure is placed on the solution, then the diffusion pressure of the solvent molecules from the solution and solvent will become equal and there will be no differential flow but a dynamic equilibrium.

In order to have osmosis it is *not* necessary to have a pure solvent against a solution. Two solutions of different concentration will also exhibit the phenomenon of osmosis with solvent from the dilute solution differentially flowing into the more concentrated solution.

Osmotic pressure is much like gas pressure in that at constant temperature the osmotic pressure is directly proportional to the molal concentration of the solution; at constant concentration the osmotic pressure is directly proportional to the absolute temperature. As an approximation the osmotic pressure can be calculated from the ideal

gas law equation,  $PV = \frac{g}{M} \times RT$ , where  $P$  is the osmotic pressure in

atmospheres,  $V$  is the volume of the solution in litres containing  $g$  grams of solute of molecular weight  $M$ ,  $R$  is the gas constant, 0.08203 litre-atmosphere per degree per mole, and  $T$  is the absolute (Kelvin) temperature.

The osmotic pressure of solutions is one of the colligative properties of a solution and is therefore closely related to changes in vapour pressure, depressions of freezing points, and elevations of boiling

points. The colligative properties of solutions can be utilized to obtain the molecular weights of non-electrolytes (see Molecules and Molecular Weights). (See Colloid Chemistry.)

**Electro-Osmosis**, that is, osmosis supplemented by means of the electric current, finds application in many industries, and depends upon the fact that, under this influence, liquid conductors tend to filter through porous or semipermeable partitions with a speed independent of their thickness and only varying with their nature and section. Colloidal substances, which swell in water, often exhibit great absorbing capacities, and are capable of superficially fixing the molecules or ions of bodies dissolved in the liquids in which they may be immersed in a chemical manner, and it is this property which is utilized, for example, in the electro-osmotic process of tanning with chromium salts. This phenomenon is due to the fact that at the contact boundary between a solid and a liquid, each assumes an electrical charge of opposite character; in some cases the solid gains the positive charge, while the liquid becomes electro-negative; the electrification of the granules and liquid being due to the utilization of the ions formed by the salts always present in water.

Electrophoresis means the migration of a sol or the dispersed phase towards anode or cathode (the electrodes) under influence of electric charge due to the production of potential differences at the interface between liquid and solid; positive sols such as the metallic hydroxides pass to the cathode, and negative ones such as metals to the anode.

See Silica, Clay, Peat, Rubber, and Tanning.

**OSSEIN** — A variety of gelatin or albuminous substance present in and prepared from bones. (See Bones, and Gelatin.)

**OSTEOLITE** — A form of apatite. (See Apatite, and Calcium (Phosphate).)

**OSTWALD'S DILUTION LAW** — See Solution.

**OSTWALD'S RULE** — When a substance which can exist in more than one modification is formed, the least stable one is first formed; this may then change sooner or later into the stable one.

**OTOBA BUTTER** — The fat expressed from the fruit of *Myristica otoa*, containing glycerides and some sesquiterpenes; sap. v., 185; and m.p., 34° C. (See Mace, and Nutmeg.)

**OTTO OF ROSES** — See Attar of Roses.

**OUABAIN (Strophanthin-G)** ( $C_{29}H_{44}O_{12} \cdot 8H_2O$ ) — A colourless, crystalline glycoside obtained from the seeds of *Strophanthus gratus* or from the wood of *Acokanthera Schimperi*, sparingly soluble in water; soluble in alcohol; insoluble in ether and chloroform; m.p. about 200° C., after drying *in vacuo* at 100° C. Ouabain increases the activity of cardiac muscle, causing more effective filling of the heart and a greater output; it is used in medicine for the treatment of auricular fibrillation

and cardiac dropsy. The potency of ouabain is approximately twice that of strophanthin-K, obtained from the seeds of *Strophanthus kombe*. (See Digitalis, and Strophanthus.)

**OURICURÍ OIL** — The leaves of the ouricurí palm tree of Brazil produce a wax similar to carnauba wax, and the kernels a pale yellow oil, used as edible oil and for soap making. The kernels yield 50 to 60 per cent. of oil.

**OX GALL** — The bile obtained from the gall bladder of oxen, a ropy, mucous, transparent liquid of greenish-brown colour used for wool-scouring, and in the engraving and lithographing trades. (See Bile.)

**OXALATES** — Compounds of oxalic acid with metals and bases. The alkaline oxalates are soluble in water, but the others are for the most part insoluble. Ferrous oxalate is a convenient substance from which to obtain ferrous oxide upon heating, also stannous oxalate similarly yields stannous oxide. Calcium oxalate possesses such a low solubility that its formation is one of the most satisfactory tests for calcium ion or oxalate ion. It is insoluble in acetic acid (low hydrogen-ion concentration) and soluble in hydrochloric acid (high hydrogen-ion concentration).

**OXALIC ACID** ( $\text{COOH}.\text{COOH}, 2\text{H}_2\text{O}$ ) may be regarded as an oxidation product of the dihydric alcohol, ethylene glycol ( $\text{CH}_2\text{OH}.\text{CH}_2\text{OH}$ ), and is a dibasic acid. It occurs combined with potassium as oxalate ( $\text{K}_2\text{C}_2\text{O}_4$ ) in many plants, particularly in wood sorrel (*Oxalis acetosella*) and varieties of *Rumex*; in the free state in some varieties of *Boletus*, and as calcium oxalate in rhubarb root and many lichens and fungi. It is also found in the form of calcium oxalate among the products of changes induced by the growth of *Aspergillus niger* in sugar solutions containing salts including calcium carbonate. Urinary deposits and calculi also often contain the calcium salt.

Oxalic acid can be made by the action of nitric acid upon sugar, or by fusing a mixture of cellulose (sawdust) with potassium or sodium hydroxide at from  $200^\circ$  to  $230^\circ$  or  $240^\circ$  C. in iron vessels: the fused mass is afterwards extracted with water, and upon addition of calcium chloride, insoluble calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) is precipitated, and from this compound oxalic acid is obtained by treatment with sulphuric acid. The soft woods give a better yield of oxalic acid than the hard woods. It can similarly be obtained from sugar and starch.

The "formate" process of making oxalic acid, which has practically superseded the older sawdust method, consists of heating sodium hydroxide with carbon monoxide under pressure, thus producing sodium formate ( $\text{NaCHO}_2$ ), and when this is heated sodium oxalate is produced:  $2\text{HCOONa} = \text{COONa} + \text{H}_2$ , the reaction being slightly



endothermic. By adding a calcium salt to the solution of sodium oxalate, calcium oxalate is precipitated, and when that compound is treated with sulphuric acid, the oxalic acid is set free, the resulting calcium sulphate can be separated by filtration, and the solution evaporated to obtain crystals of oxalic acid. As an alternative the sodium oxalate is treated with lime and producer gas at  $200^{\circ}\text{C}$ . and under a pressure of 15 atmospheres, yielding sodium formate and calcium oxalate.

A method of preparing the anhydrous form from the hydrated acid by distillation with toluene has been described by J. R. Partington.

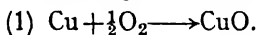
Oxalic acid is very poisonous, crystallizes in large transparent rhombic prisms, which slowly effloresce in the air, is soluble in water and to some extent in alcohol. The hydrated acid melts at  $98^{\circ}\text{C}$ . in its water of crystallization; at  $100^{\circ}\text{C}$ . it loses this water and becomes anhydrous, while at  $110^{\circ}$  to  $120^{\circ}\text{C}$ . it decomposes and yields a mixture of carbon monoxide and dioxide together with water.

Oxalic acid is used in the dyestuffs and textile industries; in bleaching straw, wood, cotton-linters, etc.; in preparing inks, and for various other applications, including brass cleaning. Ammonium oxalate  $((\text{NH}_4)_2\text{C}_2\text{O}_4, \text{H}_2\text{O})$  is used as an analytical reagent, while the potassium binoxalate  $(\text{KHC}_2\text{O}_4, \text{H}_2\text{O})$  (salt of sorrel) is used for cleaning brass and removing ink stains. The ferrous potassium oxalate  $(\text{FeK}_2(\text{C}_2\text{O}_4)_2)$  is a powerful reducing agent, and is used in photography as "oxalate developer." Dried sodium oxalate is used as a standard in volumetric analysis against permanganate solution.

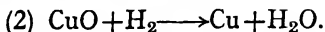
**OXAMIDE** — See Amides.

**OXIDASES** — See Enzymes.

**OXIDATION-REDUCTION** — A substance which undergoes combination with oxygen, an oxidizing agent, is said to be oxidized, and the process which takes place is called oxidation. For example:



The copper is said to be oxidized by oxygen, the oxidizing agent, in the process called oxidation. In a like manner reduction is the removal of oxygen from a compound by a reducing agent and the substance that loses the oxygen is said to be reduced. For example:



Hydrogen, the reducing agent, reduces copper oxide to copper by the process called reduction. It should be noted that reduction is the reverse of oxidation, and that each is accompanied by the other. An examination of reaction (2) above shows this well. It reveals the fact that hydrogen, the reducing agent, has become oxidized because it has combined with oxygen to form water, which process is oxidation.

The terms oxidation and reduction are not limited to reactions where oxygen is gained or removed. When reaction (2) is examined more closely it is apparent that copper in copper oxide has a valence of plus two,  $\text{Cu}^{++}$ , and as metallic copper it has a valence of zero. In the reduction of copper oxide by hydrogen, copper exhibits the following

change,  $\text{Cu}^{++} + 2 \text{ electrons} \rightarrow \text{Cu}^0$ . The doubly charged copper ion has gained two electrons to become metallic copper—this is also *reduction*. While the above change occurs hydrogen element is converted into hydrogen ion carrying one unit positive charge,  $\text{H}^+$ , i.e.,  $\text{H}_2 - 2 \text{ electrons} \rightarrow 2\text{H}^+$ —this is *oxidation*. (In this reaction the oxygen has not changed valence in changing from copper oxide to hydrogen oxide (water).)

An examination of equation (1) shows that copper loses two electrons to become doubly charged copper,  $\text{Cu}^{++}$ —*oxidation*; and at the same time oxygen gains two electrons to become doubly charged oxygen,  $\text{O}^{--}$ —*reduction*.

Now consider the reaction between copper and chlorine,



Again copper loses two electrons to become  $\text{Cu}^{++}$  ion, while chlorine gains an electron to become  $\text{Cl}^-$  ion. This reaction is also oxidation and reduction—but there is no oxygen element in the reaction. Thus, in the most general cases of oxidation–reduction there need not be any oxygen element taking part in the reaction.

By defining oxidation as the loss of electrons and reduction as the gaining of electrons it should be possible to carry out oxidation–reduction reactions by means of the electric current. For example:  $\text{CuCl}_2 + \text{electric current} \rightarrow \text{Cu} + \text{Cl}_2$ . The copper is deposited at the cathode and chlorine is liberated at the anode. Since copper is reduced in this reaction (gained electrons), the cathode is the reducing electrode—the source of the electrons. The chloride ion is oxidized to chlorine (lost electrons) at the anode, therefore the anode is the oxidation electrode—picks up or removes electrons from substances. (Thus the terms anodic oxidation and cathodic reduction.) It should be noted that in any oxidation–reduction reaction the same number of electrons lost in the oxidation are gained in the reduction.

Oxidation and reduction always occur simultaneously. The reducing agent always undergoes oxidation while it is reducing the oxidizing agent, and the oxidizing agent always undergoes reduction while it is oxidizing the reducing agent.

The tendency of substances to lose or gain electrons is a characteristic of the substance. Some substances have this tendency to a greater degree than other substances. This tendency can be measured by means of an electrical potential (E.M.F.) and the substances can be arranged in a relative order (see Electricity (Electromotive Series)).

Oxidation–reduction reactions when properly controlled are of great service. They include such important operations as photosynthesis, digestion, respiration, explosions, electrochemical depositions, synthesis of organic compounds, for example, oxidation of alcohol to acetic acid, methyl alcohol from carbon monoxide and hydrogen, hydrogenation of fatty oils, making of nitrobenzene, aniline, and dyes. Many industries owe their existence to oxidation–reduction reactions, i.e., sulphuric acid, Haber process for ammonia, conversion of ammonia to nitric acid, the electrolytic metal industries, and others.

*References* : Nichols Medal Address, by W. M. Clark on "A Little of the Perspective of Acid-Base and Oxidation-Reduction Equilibrium" (*Ind. Eng. Chem.*, **28**, 620 (1936)); *Mechanism of Oxidation*, by H. Wieland (Oxford Univ. Press); *The Physical Chemistry of Electrolytic Solutions*, by Harned and Owen (Reinhold Publishing Corp., New York); *Chemistry for the Executive*, by Ralph K. Strong (Reinhold Publishing Corp., New York).

**OXIDES** — See Bases, Chemical Compounds, Oxygen, and accompanying Table.

### OXIDES, ARRANGED BY PERIODIC GROUPS

Table showing Principal Members, with Corresponding Formulas, Densities, and Melting Points

Arranged by the Editor.

NOTES : For Heats of Formation see ELEMENTS, Table of Data.

For Periodic Group Arrangement see chart facing page 1.

Element	Oxide	Formula	Density	Melting Point °C.
Hydrogen	Monoxide (Water)	H <sub>2</sub> O	0.998 at 20° C.	0-0
	Peroxide (Dioxide)	H <sub>2</sub> O <sub>2</sub>	1.4	-1.7
<b>GROUP O</b>	None			
<b>GROUP IA</b>				
Lithium	Oxide	Li <sub>2</sub> O	2.0	>1700
Sodium	Oxide	Na <sub>2</sub> O	2.3	
	Peroxide (Dioxide)	Na <sub>2</sub> O <sub>2</sub>	2.8	460 decom.
Potassium	Oxide	K <sub>2</sub> O	2.3	
	Peroxide (Dioxide)	K <sub>2</sub> O <sub>2</sub>		490
	Tetroxide	K <sub>2</sub> O <sub>4</sub>		>280
Rubidium	Oxide	Rb <sub>2</sub> O	3.7	400 decom.
	Peroxide (Dioxide)	Rb <sub>2</sub> O <sub>2</sub>	3.7	600
	Trioxide	Rb <sub>2</sub> O <sub>3</sub>	3.5	>500
	Tetroxide	Rb <sub>2</sub> O <sub>4</sub>	3.1	280
Cesium	Oxide	Cs <sub>2</sub> O	4.4	360-400 decom.
	Peroxide (Dioxide)	Cs <sub>2</sub> O <sub>2</sub>	4.3	400
	Trioxide	Cs <sub>2</sub> O <sub>3</sub>	4.3	400
	Tetroxide	Cs <sub>2</sub> O <sub>4</sub>	3.8	515 in O <sub>2</sub>
Francium	—	—		
<b>GROUP IIA</b>				
Beryllium	Oxide	BeO	3.0	2570
Magnesium	Oxide	MgO	3.7	2800
	Peroxide	MgO <sub>2</sub>		
Calcium	Oxide	CaO	3.4	2570
	Peroxide (Dioxide)	CaO <sub>2</sub>		275 (O <sub>2</sub> off)
Strontium	Oxide	SrO	4.7	2430
	Peroxide (Dioxide)	SrO <sub>2</sub>	4.6	(O <sub>2</sub> off)
Barium	Oxide	BaO	5.7	1920
	Peroxide (Dioxide)	BaO <sub>2</sub>	5.0	800 (O <sub>2</sub> off)
Radium	—	—		

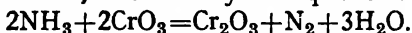
Element	Oxide	Formula	Density	Melting Point °C.
<b>GROUP IIIA</b>				
Boron	Oxide (Trioxide)	$B_2O_3$	1.8	575
Aluminium	Oxide (Trioxide)	$Al_2O_3$	4.0	2050
Scandium	Oxide (Trioxide)	$Sc_2O_3$	3.9	
Yttrium	Oxide (Trioxide)	$Y_2O_3$	4.8	2410
Lanthanum	Oxide (Trioxide)	$La_2O_3$	6.5	2315
Cerium	Cerous oxide (Trioxide)	$Ce_2O_3$	7.0	200 decom.
	Ceric oxide (Dioxide)	$CeO_2$	7.3	1950
Praseodymium	Oxide (Trioxide)	$Pr_2O_3$	6.9	
	Dioxide	$PrO_2$		
	Tetroxide	$PrO_4$	6.0	
	Oxide (Trioxide)	$Nd_2O_3$	7.2	
Neodymium				
Promethium	—	—		
Samarium	Oxide (Trioxide)	$Sm_2O_3$	7.7	1350
Europium	Oxide (Trioxide)	$Eu_2O_3$	7.4	
Gadolinium	Oxide (Trioxide)	$Gd_2O_3$	7.4	
Terbium	Oxide (Trioxide)	$Tb_2O_3$		
	Peroxide	$Tb_2O_7$		
	Oxide (Trioxide)	$Dy_2O_3$	7.8	
Dysprosium	Oxide (Trioxide)	$Ho_2O_3$		
Holmium	Oxide (Trioxide)	$Er_2O_3$	8.6	
Erbium	Oxide (Trioxide)	$Tm_2O_3$		
Thulium	Oxide (Trioxide)	$Yb_2O_3$	9.2	
Ytterbium	Oxide (Trioxide)	$Lu_2O_3$		
Lutetium	Oxide (Trioxide)			
<b>GROUP IVA</b>				
Carbon	Dioxide	$CO_2$	1.1 at $-37^\circ C.$	$-57$ at 5.2 atm.
	Monoxide	CO	0.8 at $-190^\circ C.$	$-207$
	Suboxide	$C_3O_2$	1.1	$-111$
Silicon	Oxide (Dioxide)	$SiO_2$	Quartz 2.65	Quartz 1625
			Tridymite 2.30	Tridymite 1670
			Christobalite 2.32	Christobalite 1710
			Anatase 3.84	
			Brookite 4.17	
Titanium	Oxide (Dioxide)	$TiO_2$	Rutile 4.26	Rutile 1640
			$Ti_2O_3$ 4.6	2130
	Sesquioxide	$Ti_2O_3$	4.9	1750
	Monoxide	$TiO$		
	Peroxide	$TiO_4$		
Zirconium	Oxide (Dioxide)	$ZrO_2$	5.7	2700
Hafnium	Oxide (Dioxide)	$HfO_2$	9.7	2810
Thorium	Oxide (Dioxide)	$ThO_2$	9.7	$>2800$
	Peroxide	$Th_2O_7$		
<b>GROUP VB</b>				
Vanadium	Pentoxide	$V_2O_5$	3.4	690
	Tetroxide	$V_4O_{14}$	4.3	1965
	Trioxide	$V_2O_3$	4.9	1970
	Dioxide	$V_2O_4$	5.8	(O, on)

Element	Oxide	Formula	Density	Melting Point °C.
<b>GROUP VB</b>				
—cont.				
Columbium (Niobium)	Pentoxide	$\text{Cb}_2\text{O}_5$	4.5	1520
	Dioxide	$\text{CbO}_2$		
	Monoxide	$\text{CbO}$	6.3	
Tantalum	Pentoxide	$\text{Ta}_2\text{O}_5$	8.7	1470 decom.
	Tetroxide	$\text{Ta}_2\text{O}_4$		( $\text{O}_2$ on)
	Dioxide	$\text{Ta}_2\text{O}_3$		( $\text{O}_2$ on)
Protactinium	—	—		
<b>GROUP VIB</b>				
Chromium	Trioxide (Chromic anhydride)	$\text{CrO}_3$	2.7	190 decom.
	Dioxide [oxide]	$\text{CrO}_2$	4.0	300 ( $\text{O}_2$ off)
	Chromic oxide (Sesquioxide)	$\text{Cr}_2\text{O}_3$	5.2	1990
	Chromous oxide (Monoxide)	$\text{CrO}$		
Molybdenum	Trioxide	$\text{MoO}_3$	4.5	795
	Dioxide	$\text{MoO}_2$	4.5	
	Sesquioxide	$\text{Mo}_2\text{O}_3$		
Tungsten	Trioxide	$\text{WO}_3$	7.2	1475
	Dioxide	$\text{WO}_2$	12.1	
Uranium	Trioxide (Uranyl oxide)	$\text{UO}_3$	5.9	decom.
	Triuranium octaoxide	$\text{U}_3\text{O}_8$	7.3	decom.
	Dioxide	$\text{UO}_2$	10.9	2175
<b>GROUP VIIB</b>				
Manganese	Heptoxide	$\text{Mn}_2\text{O}_7$	2.4	—20
	Trioxide	$\text{MnO}_3$		( $\text{O}_2$ off)
	Dioxide [oxide]	$\text{MnO}_2$	5.0	535 ( $\text{O}_2$ off)
	Manganic oxide (Sesquioxide)	$\text{Mn}_2\text{O}_3$	4.5	1080 ( $\text{O}_2$ off)
	Trimanganese tetroxide	$\text{Mn}_3\text{O}_4$	4.9	1705
	Manganous oxide (Monoxide)	$\text{MnO}$	5.4	1650
Technetium	—	—		
Rhenium	Heptoxide	$\text{Re}_2\text{O}_7$	8.2	220
	Dioxide	$\text{ReO}_2$		
	Peroxide (Tetroxide)	$\text{ReO}_4$	8.4	150 decom.
<b>GROUP VIII</b>				
Iron	Ferric oxide (Sesquioxide)	$\text{Fe}_2\text{O}_3$	5.2	1560 decom.
	Ferro-ferric oxide (Triiron tetroxide)	$\text{Fe}_3\text{O}_4$	5.2	1540 decom.
	Ferrous oxide	$\text{FeO}$	5.7	1420
Cobalt	Cobaltic oxide (Sesquioxide)	$\text{Co}_2\text{O}_3$	5.2	900 decom.
	Cobalto-cobaltic oxide (Tricobalt tetroxide)	$\text{Co}_3\text{O}_4$	6.1	
	Cobaltous oxide	$\text{CoO}$	5.7	1800 decom.
Nickel	Nickelic oxide (Sesquioxide)	$\text{Ni}_2\text{O}_3$	4.8	600 ( $\text{O}_2$ off)
	Nickelo-nickelic oxide (Trinickel tetroxide)	$\text{Ni}_3\text{O}_4$		
	Nickelous oxide	$\text{NiO}$	7.5	400 ( $\text{O}_2$ on)
Ruthenium	Tetroxide	$\text{RuO}_4$	3.3	26
	Pentoxide	$\text{Ru}_2\text{O}_5$		360 ( $\text{O}_2$ off)
	Nonoxide	$\text{Ru}_2\text{O}_3$		440 ( $\text{O}_2$ off)
	Dioxide	$\text{RuO}_2$	7.0	decom.
	Trioxide (Sesquioxide)	$\text{Ru}_2\text{O}_3$		

Element	Oxide	Formula	Density	Melting Point °C.
<b>GROUP VIII</b>				
— <i>cont.</i>				
Rhodium	Dioxide	RhO <sub>2</sub>		
	Trioxide (Sesquioxide)	Rh <sub>2</sub> O <sub>3</sub>		>1100 decom.
	Monoxide	RhO		
Palladium	Dioxide	PdO <sub>2</sub>		200 (O <sub>2</sub> off)
	Monoxide	PdO	8.3	750 decom.
	Suboxide	Pd <sub>2</sub> O		decom.
Osmium	Tetroxide	OsO <sub>4</sub>	4.9	40
	Dioxide	OsO <sub>2</sub>	7.9	650 decom.
	Trioxide (Sesquioxide)	Os <sub>2</sub> O <sub>3</sub>		decom.
	Monoxide	OsO		
Iridium	Dioxide	IrO <sub>2</sub>	3.2	decom.
	Trioxide (Sesquioxide)	Ir <sub>2</sub> O <sub>3</sub>		400 (O <sub>2</sub> off)
Platinum	Dioxide (Platinic oxide)	PtO <sub>2</sub>		450
	Platino-platinic oxide (Triplatinum tetroxide)	Pt <sub>3</sub> O <sub>4</sub>		decom.
	Monoxide (Platinous oxide)	PtO	14.9	550
<b>GROUP IB</b>				
Copper	Cupric oxide	CuO	6.4	1025 decom.
	Cuprous oxide	Cu <sub>2</sub> O	6.0	1235
	Suboxide	Cu <sub>4</sub> O		decom.
Silver	Oxide	Ag <sub>2</sub> O	7.1	300 decom.
	Peroxide	Ag <sub>2</sub> O <sub>2</sub>	7.4	>100 decom.
Gold	Auric oxide (Sesquioxide)	Au <sub>2</sub> O <sub>3</sub>		160 (O <sub>2</sub> off)
	Dioxide	Au <sub>2</sub> O <sub>2</sub>		180 decom.
	Aurous oxide (Monoxide)	Au <sub>2</sub> O	3.6	205 (O <sub>2</sub> off)
<b>GROUP IIB</b>				
Zinc	Oxide	ZnO	5.5	>1800
	Peroxide	ZnO <sub>2</sub>	1.6	
Cadmium	Oxide	CdO	7.0–8.2	900 decom.
	Suboxide	Cd <sub>2</sub> O	8.2	decom.
Mercury	Mercuric oxide	HgO	11.1	100 decom.
	Mercurous oxide	Hg <sub>2</sub> O	9.8	100 decom.
<b>GROUP IIIB</b>				
Gallium	Trioxide (Sesquioxide)	Ga <sub>2</sub> O <sub>3</sub>	6.4	1900
	Suboxide	Ga <sub>2</sub> O	4.8	>660
Indium	Trioxide (Sesquioxide)	In <sub>2</sub> O <sub>3</sub>	7.2	850 decom.
	Monoxide	InO		
	Suboxide	In <sub>2</sub> O	7.0	
Thallium	Thallic oxide (Sesqui- oxide)	Tl <sub>2</sub> O <sub>3</sub>	9.7–10.2	720
	Thallous oxide	Tl <sub>2</sub> O		300
<b>GROUP IVB</b>				
Germanium	Dioxide	GeO <sub>2</sub>	4.7–6.2	1100
	Monoxide	GeO		710 subl.
Tin	Stannic oxide (Dioxide)	SnO <sub>2</sub>	7.0	1125 decom.
	Stannous oxide (Mon- oxide)	SnO	6.4	800 decom.
Lead	Dioxide	PbO <sub>2</sub>	9.4	290 decom.
	Trilead tetroxide	Pb <sub>3</sub> O <sub>4</sub>	9.1	500 decom.
	Plumbic oxide (Sesqui- oxide)	Pb <sub>2</sub> O <sub>3</sub>		370 decom.
	Plumbous oxide (Mon- oxide)	PbO	8.0–9.5	890
	Suboxide	Pb <sub>2</sub> O	8.3	decom.

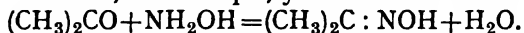
Element	Oxide	Formula	Density	Melting Point °C.
<b>GROUP VA</b>				
Nitrogen	Pentoxide	$N_2O_5$	1.6	30
	Tetroxide (Dioxide)	$N_2O_4$ ( $NO_2$ )	1.4	-9.3
	Trioxide	$N_2O_3$	1.4	-102
	Nitric oxide	NO	1.3	-164
	Nitrous oxide	$N_2O$	at -150° C.	-102
			at -89° C.	
Phosphorus	Pentoxide (Phosphoric oxide)	$P_2O_5$	2.4	250 subl.
	Tetroxide	$P_2O_4$	2.5	>100
	Trioxide (Phosphorous oxide)	$P_2O_3$	2.1	24
Arsenic	Pentoxide	$As_2O_5$	4.1	315 decom.
Antimony	Trioxide (Arsenious oxide)	$As_2O_3$	3.9	193 subl.
	Pentoxide (Antimonic oxide)	$Sb_2O_5$	3.8	380 ( $O_2$ off)
	Tetroxide	$Sb_2O_4$	4.1	930 ( $O_2$ off)
	Trioxide (Antimonous oxide)	$Sb_2O_3$	5.2-5.7	655
Bismuth	Pentoxide (Bismuthic oxide)	$Bi_2O_5$	5.1	150 ( $O_2$ off)
	Tetroxide (Dioxide)	$Bi_2O_4$ ( $BiO_2$ )	5.6	305 ( $O_2$ off)
	Trioxide (Bismuthous oxide)	$Bi_2O_3$	8.2-8.9	840
<b>GROUP VIA</b>				
Oxygen	Oxygen	$O_2$	1.14	-218.8
	Ozone	$O_3$	at -183° C. 1.71	-251
Sulphur	<i>alpha</i> -Sulphur trioxide	$SO_3$	1.9	17
	<i>beta</i> -Sulphur trioxide	$SO_3$	2.0	62
	Dioxide	$SO_2$	1.4	-73
			at 0° C.	
Selenium	Heptoxide	$S_2O_7$		0
	Sesquioxide	$S_2O_3$		70 decom.
	Trioxide	$SeO_3$	3.6	120 decom.
Tellurium	Dioxide	$SeO_2$	4.0	340
	Trioxide	$TeO_3$	5.1	decom.
	Dioxide	$TeO_2$	5.8	
	Monoxide	TeO		( $O_2$ on)
Polonium	—	—		
<b>GROUP VIIA</b>				
Fluorine	Oxide	$F_2O$	1.9	-224
Chlorine			at -224° C.	
	Heptoxide	$Cl_2O_7$		-91
	Tetroxide	$ClO_4$		
	Dioxide	$ClO_2$	2.4	-76
			at 10° C.	
	Monoxide	$Cl_2O$		-20
Bromine	—	—		
Iodine	Pentoxide	$I_2O_5$	4.8	300 decom.
	Dioxide	$IO_2$	4.2	130 decom.
Astatine	—	—		

**OXIDIZING AGENTS** — Chemical substances which are capable of introducing or giving up oxygen to other substances having an affinity for it, including air, hypochlorous acid, oxygen, ozone, and many substances rich in oxygen, as, for example, potassium permanganate ( $\text{KMnO}_4$ ), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ ), chromic anhydride ( $\text{CrO}_3$ ), nitric acid ( $\text{HNO}_3$ ), and the various peroxides. For instance, gaseous ammonia is oxidized by chromic anhydride, which substance is reduced thereby to sesquioxide, as shown by the equation :



(See Anti-Oxidants, and Oxidation-Reduction.)

**OXIMES** — A series of bodies obtained from aldehydes and ketones by condensation of the carbonyl group ( $>\text{CO}$ ) with hydroxylamine ( $\text{NH}_2\text{OH}$ ). Acetone, for example, yields acetone oxime :



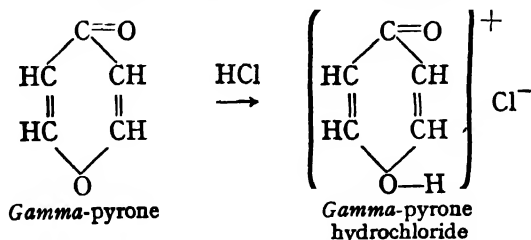
Many of the oximes possess characteristic melting-points, which are of service in the matter of identifying the original aldehydes and ketones.

Oxime of	Melting Point, ° C.
Acetaldehyde .. ..	47
Acetone .. ..	60
Acetophenone .. ..	59
Benzaldehyde, anti .. ..	35
Benzaldehyde, syn .. ..	129
Benzophenone .. ..	143
Benzoquinone (monoxime) .. ..	125
Benzoquinone (1, 4-dioxime) .. ..	240 (decomp.)

Oxime formation is made use of in the estimation of carbonyl compounds in, for example, volatile oils. The oil is treated with an excess of alcoholic solution of hydroxylamine hydrochloride, when an oxime is formed and the equivalent of hydrochloric acid liberated ; the latter is titrated with alcoholic potash (see *British Pharmacopœia*, 1948, p. 764).

**“OXOID”** — Proprietary trade-name for a range of glandular and therapeutic preparations.

**OXONIUM COMPOUNDS (Salts)** resemble ammonium salts in which nitrogen is replaced by oxygen, as if a substance oxonium hydroxide ( $\text{H}_3\text{O}.\text{OH}$ ) were the parent. *Gamma*-pyrones form crystalline salts with acids and the accepted structural explanation is —



Ethers, for example, dimethyl ether, are known to form oxonium compounds, such as  $(\text{CH}_3)_2\text{O}.\text{HCl}$ .

**OXOPHENARSINE** — See Arsphenoxide.

**OXO REACTION** — The addition of hydrogen and carbon monoxide to an olefin bond in the presence of a catalyst at a pressure of 100 to 300 atmospheres and a temperature of 120° to 180° C. The products are the oxygen function compounds, namely, aldehydes and alcohols. The reaction was first observed in 1930 by David F. Smith, of the U.S. Bureau of Mines upon passing ethylene, carbon monoxide, and hydrogen over a cobalt catalyst. It was applied in Germany to obtain high molecular weight alcohols, and is used in the U.S.A. to produce isooctyl alcohol from heptenes, and 3,5,5-trimethylhexanol from diisobutylene. The catalyst is stated to be dicobalt octacarbonyl or cobalt carbonyl hydride.

**OXY-ACETYLENE FLAME** — The complete reaction is thus represented :



so that one volume of acetylene requires  $2\frac{1}{2}$  volumes of pure oxygen for complete combustion. The temperature is from 3,100° to 3,300° C., and the flame is used for high-temperature cutting and welding.

**OXYACIDS (Oxacids)** — Acids which contain oxygen as a constituent, such as cyanic acid (HCNO), chloric acid (HClO<sub>3</sub>), nitric acid (HNO<sub>3</sub>), and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>).

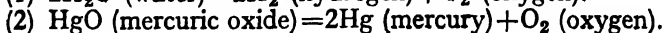
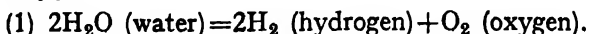
**OXYCHLORIDES** — Compounds containing both oxygen and chlorine in combination with some other element—for example, magnesium oxychloride MgCl<sub>2</sub>·5MgO, the antimony compounds SbOCl<sub>3</sub> and SbO<sub>2</sub>Cl, and phosphorus oxychloride (POCl<sub>3</sub>).

**OXYDASES** — See Enzymes.

**OXYSALTS** — Salts of oxyacids, such as carbonates, sulphates, nitrates, phosphates, etc.

**OXYGEN (O) and its Compounds, and OZONE** — Atomic Weight, 16·0000 (Standard of reference). See Elements for other data; and Oxides. Oxygen was originally obtained by heating the red oxide of mercury in the concentrated rays of the sun through the medium of a powerful lens. In combination with hydrogen, it exists in water (making up eight-ninths of its weight), and it has been roughly estimated to form nearly one-half by weight of the various rocks of which the earth's crust is composed.

Oxygen gas is not only yielded (1) by electrolysis of water and (2) by heating the red oxide of mercury, but a number of (3) the higher oxides, of which manganese dioxide and lead dioxide are typical, and some of (4) the oxysalts, for example, potassium perchlorate, chlorate, and permanganate, yield oxygen upon heating. And (5) sodium peroxide *plus* water is an excellent method for the laboratory preparation of oxygen.



- (3)  $3\text{MnO}_2$  (manganese dioxide) =  $\text{Mn}_3\text{O}_4$  (trimanganese tetroxide) +  $\text{O}_2$  (oxygen).  
 $2\text{PbO}_2$  (lead dioxide) =  $2\text{PbO}$  (lead monoxide) +  $\text{O}_2$  (oxygen).  
 $2\text{BaO}_2$  (barium peroxide) =  $2\text{BaO}$  (barium oxide) +  $\text{O}_2$  (oxygen).  
 $*2\text{H}_2\text{O}_2$  (hydrogen peroxide) =  $2\text{H}_2\text{O}$  (water) +  $\text{O}_2$  (oxygen), in the presence of finely divided manganese dioxide (catalyst).  
 (4)  $*\text{KClO}_4$  (potassium perchlorate) =  $\text{KCl}$  (potassium chloride) +  $2\text{O}_2$  (oxygen).  
 $2\text{KClO}_3$  (potassium chlorate) =  $2\text{KCl}$  (potassium chloride) +  $3\text{O}_2$  (oxygen) (hazardous in the presence of organic material).  
 (5)  $*2\text{Na}_2\text{O}_2$  (sodium peroxide) +  $2\text{H}_2\text{O}$  (water) =  $4\text{NaOH}$  (sodium hydroxide) +  $\text{O}_2$  (oxygen).

The oxygen of the air (of which it constitutes about one-fifth) can be separated from the associated nitrogen by chemical means, or its liquefaction can be effected by pumping it at a very low temperature and under great pressure into vessels made exceedingly cold. From liquefied air the two gases, nitrogen and oxygen, pass again into the state of vapour at different temperatures. Nitrogen boils at  $-195.8^\circ\text{C}$ . under atmospheric pressure, and oxygen at  $-183.0^\circ\text{C}$ .; so that it is possible to boil off the nitrogen—or most of it—before the oxygen, and this process is used for the manufacture of both liquid oxygen and nitrogen on a large scale. Fractions containing oxygen well above the concentration found in air but too low in oxygen for selling as such may find extensive use for combustion reactions in metallurgical and other high-temperature fields. On the uses of rich oxygen the following references are submitted: "Oxygen—Past, Present and Prospects" (*Chem. Eng.*, Jan., 1947); "Impact of Tonnage Oxygen on American Chemical Industry," by C. R. Downs (*Chem. Eng.*, Aug., 1948); "Production of Oxygen for Industrial Purposes," by W. E. Lobo (*Chem. Eng.*, Jan., 1947); "Oxygen Manufacture," by Harding Bliss and Barnett F. Dodge (*Chem. Eng.*, Jan., Feb., 1949); "Developments in Oxygen Production," by J. Henry Rushton and E. P. Stevenson (*Trans. Amer. Inst. Chem. Eng.*, Feb., 1947); "The Application of Oxygen in the Operation of the Blast Furnace," by D. D. Howat (*Blast Furn. and Steel Plant*, May, 1948); "Oxygen Enrichment of the Cupola Blast," by A. K. Higgins (*Iron Age*, April 22, 1948); "Oxygen Uses in Steel Production," by J. H. Zimmerman (*Iron and Steel Eng.*, Feb., 1948); "The Use of Oxygen in Open Hearth Furnaces," by E. C. McDonald (*Iron and Steel Eng.*, March, 1948); "Oxygen in the Steel Industry," by H. W. McQuaid and F. E. Paylis (*Iron and Steel Eng.*, April, 1948).

The various types of electrolytic cells used for the commercial production of oxygen (and hydrogen) from water are referred to under Hydrogen.

Oxygen is still liquid at  $-210^\circ\text{C}$ ., and in this form is of a pale steel-blue shade of colour and exhibits strong magnetic properties. Each cubic foot of the liquid yields 800 cubic feet of gas. Among its many applications is that of its use as an explosive when mixed with

\* Preferred laboratory methods of preparation of oxygen

combustible matter, such as sawdust or carbon. Liquefied oxygen itself is not explosive, but cartridges of paper filled with sawdust or other combustible soaked in the liquid oxygen for some five or ten minutes, when lighted in a closed space, such as a borehole made for blasting purposes, are highly explosive. A litre of oxygen used in this way is said to be the equivalent of 1 kilogram of black gunpowder and very much cheaper. (See Explosives.)

Pure oxygen gas is largely used for the treatment of certain complaints by inhalation, also for many manufacturing and trade purposes, including lead-burning, and its employment alone or in association with hydrogen or acetylene for the production of flame is used for the cutting and welding of metals. Oxygen in the atmosphere plays an exceedingly important role in the life processes, being absorbed by the hæmoglobin of the blood in the lungs. The arterial blood gives up oxygen to the tissues in the capillaries, and in the tissues the process of oxidation provides energy for animal living.

Pure oxygen gas is colourless, tasteless, and slightly soluble in water (1 volume at 0° C. dissolving 0.0489 volume of the gas), fish being dependent upon this dissolved quantity for respiration. In fact, oxygen is the only gas that is capable of supporting respiration, and the importance of oxygen in respect of respiration and combustion is referred to elsewhere. (See Air, Carbon Oxides, and Respiration.) The removal of dissolved oxygen from water used for boiler-feed purposes is of considerable importance in industry. This may be accomplished by heating or by the addition of chemicals, such as sodium sulphite, in amount about 1 pound of reagent per million gallons of water and occupying about 2 minutes.

Oxygen is unique among gases in its property of being attracted by a magnet (paramagnetism), most gases being slightly repelled. Pauling made use of this property to analyse gases for their oxygen content. The method is capable of measuring a few parts of oxygen per million of gas.

Oxygen exhibits powerful and widely spread affinities for other substances, forming various **oxides** with a great number of elements, combining with hydrogen to form water and hydrogen dioxide, and entering into the composition of an enormous number of chemical compounds. Its chemical activity is pronouncedly decreased by prolonged drying, so that it will not combine with dry carbon, sulphur, phosphorus, hydrogen, etc., at temperatures at which otherwise it would do so.

See J. R. Huffman and H. C. Urey on "Separation of Oxygen Isotopes by a Fractionating Column" (*Ind. Eng. Chem.*, **29**, 531 (1937)); Atomic Weights; and Oxides.

**Ozone** — When oxygen gas is subjected to the influence of the silent electric discharge, it is converted into what is called an allotropic state and becomes ozone. The chemical difference is that whereas the molecule of oxygen contains 2 atoms ( $O_2$ ), that of ozone contains 3 atoms ( $O_3$ ), and the properties of the two substances are perfectly distinct. An appreciable quantity of ozone is stated to result from introducing a

few drops of water into gaseous fluorine as represented by the equation :  $3F_2 + 3H_2O = 6HF + O_3$ . Ozone is also produced when phosphorus is partially immersed in water and exposed to the air—ozone is formed in the air and hydrogen dioxide ( $H_2O_2$ ) is formed in the water.

When an electric machine is giving out high-voltage discharges, as in the use of induction coils, ozone is produced in the air, and this was the method employed by Brodie in his researches concerning ozone and its properties.

A good yield of ozone is obtainable by the electrolysis of sulphuric acid of density 1.1 to 1.4 by superposed continuous and alternating electric currents, using an internally cooled anode of lead coated with lead dioxide or platinum.

There are a number of appliances for generating ozonized air, all constructed on the principle of Siemens' original design, in which surfaces of tinfoil, separated by glass (which is dielectric), are connected with the secondary terminals of an induction coil. In the "Ozonair" thin mica plates alternating with metallic gauze electrodes are used, and it yields air charged with ozone to the extent of 500 to 1,500 parts per million.

As prepared by the use of these electrical "ozonators" it is used commercially for the sterilization of drinking water, the purification of air, the decolourization of sugar, juices, syrups, etc., the bleaching of wax, textiles and other fabrics, paper pulp, sponges, and for giving drying properties to oils, varnishes, and paints, and the seasoning of wood. A current of air containing a small percentage of ozone is alleged to be capable of seasoning timber in about twenty days to a state which is reached naturally only in the course of several years.

Ozone has been liquefied (Riesenfeld and Schwab); has a m.p. of  $-251^\circ C.$ , a b.p. of  $-112^\circ C.$ , and density of 1.71 at  $-183^\circ C.$ ; in this condition it exhibits an intense blue colour and is extremely explosive. It instantly oxidizes nitrogen tetroxide to the pentoxide, as sharply indicated by the disappearance of colour.

Whereas oxygen is quite tasteless and odourless, ozone has a peculiar fish odour, is soluble in turpentine, and exhibits very superior powers as an oxidizing and bleaching agent. For example, silver does not suffer oxidation when exposed to pure oxygen, but it is rapidly attacked by ozone and becomes peroxidized; and ozone has also the power of decomposing potassium iodide, setting iodine free. By way of absolute proof that ozone and oxygen are identical in matter, it has been shown that they are mutually convertible; ozone being retransformed into oxygen by raising it to a temperature of  $246^\circ C.$ , 2 volumes of ozone thus yielding 3 volumes of oxygen. Mercury is readily attacked by ozone, and therefore cannot be used for confining it.

Ozone is not ordinarily found on the surface of the earth, but there is evidence of its presence in the upper atmosphere at high altitudes, and, doubtless, it is formed in lightning discharges when the oxygen of the air is subjected to electrical influences. It has been alleged that the high temperature of the air at great heights is due to the presence of ozone, which absorbs some 6 per cent. of the incoming solar energy.

**OXYHÆMOGLOBIN** — The compound formed in the blood by the action of inspired oxygen on its hæmoglobin constituent, which carries oxygen to the animal tissues. (See Blood, and Hæmatine.)

**OXYHYDROGEN FLAME** — Produced by burning a mixture of oxygen and hydrogen gases, when both ozone and hydrogen dioxide are said to be formed to some extent ; until superseded by the electric furnace it was used, amongst other purposes, for the manufacture of artificial rubies and sapphires. Its temperature is about 2,800° C.

“ **OXYLAN** ” — See Diphenan.

**OXYTOCIN** (“ **Pitocin** ”) — The oxytoxic principle fractionated from an aqueous extract of the posterior pituitary gland. It is used as a sterile aqueous solution to control postpartum hæmorrhage in childbirth.

**OZOKERITE** — Mineral wax of yellowish-black or green colour occurring in the vicinity of coal in Galicia, Poland, Moldavia, Utah, Wyoming, etc. ; soluble in benzol, turpentine, carbon disulphide, etc. ; consists of paraffin hydrocarbons, and used in the manufacture of candles, sealing-wax, paints, polishes, etc. ; sp. gr. 0.85 to 0.95, and m.p. varying between 65° and 80° C. By purification and bleaching it gives the ceresine wax of commerce. (See Waxes.)

**OZONE** — See Oxygen (Ozone).

**OZONIDES** — Combinations of ozone with unsaturated compounds, the ozone adding on at the double bond ; for example, ethylene ozonide ( $C_2H_4.O_3$ ). On treatment with water the ozonides decompose with the formation of two carboxylic acids, the original unsaturated compound splitting at the double bond. From the nature of the fission products the position of the double bond in the original compound can be found, hence the method of ozonolysis has many applications in the determination of the structure of unknown compounds.

The ozonides of the metals are solid, and have metallic fractures ; mercury ozonide dissociates on trituration in air.

**p**—**Para** (see Para Compounds).

“ **P.A.B.S.** ” — See Sulphanilamide.

**PACHIMETER** — A machine for measuring the heaviness of soils, and used in the study of flour doughs.

**PACKED TOWERS** — Packed towers are extensively used in the chemical industry for distillation, gas absorption, solvent extraction, and other operations involving the counter-current contacting of two fluid phases. In all packed towers the denser fluid is introduced at the top and the less dense at the bottom. Under the influence of gravity the two fluids travel in opposite directions, being agitated and mixed by turbulence in the packing, and each leaves the tower at the opposite end to that at which it entered. Compared with bubble towers, packed towers have the advantage of cheapness and low pressure drop,

and the disadvantage that their efficiency varies greatly with the throughput. A packed tower is most efficient at a high rate of throughput and may be very inefficient at a low rate; it should therefore be carefully sized to suit the intended duty.

Tower packings are of two types, regular and random. Regular packings consist of pieces all of the same shape stacked in a regular pattern inside the tower. The simplest example is composed of bricks or tiles set on edge at regular intervals; these, however, have a relatively low specific surface (surface per unit volume), and many kinds of stoneware shapes are available which offer a greater specific surface. A special type of regular packing used in distillation is the Stedman, made from superimposed sheets of metal gauze stamped with an indented pattern. It has a high efficiency for a given height, but is expensive.

Random packings are the more commonly used, and consist of pieces dumped at random in the tower. The simplest and cheapest random packings are broken stone, brick, or coke; these have the drawback that there is comparatively little free space in the tower, and the pressure drop is consequently high. Raschig rings are hollow cylinders of metal, stoneware, or porcelain, the height of which is equal to the external diameter. Lessing rings are similar, but have a diametrical strip to increase the specific surface. Other kinds of ring have cruciform or spiral inserts for the same reason. Berl saddles are saddle-shaped packing elements which are claimed to offer more specific surface and less back-pressure than rings. In laboratory columns glass balls, small helices of metal or glass, brass eyelets, jack chain, and various types of metal gauze packings are used.

With all random packings it is of the utmost importance that their orientation should be truly random. If rings are simply dumped into a tower they tend to take up a conical orientation which causes the descending liquid to flow preferentially towards the perimeter of the tower. There is then a tendency for most of the descending liquid to travel down the outside of the packing, and for most of the gas, vapour, or ascending liquid to travel up the centre, giving poor contact between them. One method of ensuring random orientation is to fill the tower with water before introducing the rings. Another is to add the rings in small quantities and rake the surface level after each addition.

The size of the individual packing element affects the height of packing required for a given duty. Theoretically, if the diameter of the packing element be doubled the specific surface is halved, and hence twice the height of packing should be required. In fractional distillation this is roughly true, but in absorption towers the height of packing required for a given duty is less than doubled when the diameter of the packing element is doubled. Industrial ring packings are generally from  $\frac{1}{2}$  to 2 inches in diameter, the larger sizes permitting higher fluid velocities without flooding. To maintain a uniform liquid distribution in a packed tower, the tower diameter should be not less than 8 times the diameter of the packing elements.

The efficiency of packed towers is expressed as either H.E.T.P.,

H.E.T.S. (height of equivalent theoretical plate or stage), or H.T.U. (height of transfer unit). The less the height, the greater the efficiency. A transfer unit is a section of packing producing a concentration change equal to the mean difference between the actual and equilibrium concentrations over the section. H.T.U. is the more theoretically correct unit for evaluating the performance of packed towers, but the H.E.T.P. or H.E.T.S. are sometimes more convenient. Values of these units, which are all approximately the same, may vary from a few inches to several feet, depending on the size of the packing elements, the nature and composition of the phases, and the fluid velocities. As a rough guide the H.E.T.P. of a fractionating column with random ring packing may be taken as 24 times the outside diameter of the rings.

When a packed tower is overloaded it floods; that is, the flow ceases to be counter-current, and one fluid carries the other back with it. Flooding is accompanied by a sharp increase in pressure drop. For any given velocity of one phase there is a corresponding velocity of the other which will cause flooding, and hence flooding velocities are represented by a curve relating the velocities of the two phases. Since a packed tower is most efficient when operated just below the flooding velocity, it is important that this should be known. A correlation for liquid-gas flow is given by Elgin and Weiss (*Ind. Eng. Chem.*, **31**, 435 (1930)). Useful data on liquid-liquid extraction towers are given by A. P. Colburn, *Trans. Amer. Inst. Chem. Engrs.*, **38**, 305 (1942), in the discussion of a paper by Blanding and Elgin.

*References*: T. K. Sherwood, *Absorption and Extraction* (McGraw-Hill Book Co., New York); and standard works listed under Chemical Engineering.

**PAINTS** — Mixtures of ground white-lead, red-lead, powdered aluminium, zinc oxide, titanium oxide, zinc sulphide, asbestos, lime, china clay, calcium sulphate, barium sulphate, or other mineral bases, with boiled linseed oil and turpentine (or turpentine substitute); used to prevent the rusting of iron and for the preservation of wood and other surfaces; also for artistic and decorative purposes. The preparation of iron and steel surfaces for painting is discussed by V. N. Darsey in *Ind. Eng. Chem.*, **27**, 1142 (1935); the painting of aluminium and aluminium alloy surfaces by J. D. Edwards and R. I. Wray in *Ind. Eng. Chem.*, **27**, 1145 (1935); and the painting of zinc and zinc alloy surfaces by H. A. Nelson in *Ind. Eng. Chem.*, **27**, 1149 (1935). The oxides of antimony and titanium are also used as bases for white paints, and aluminate of lead and aluminosilicate of lead have been recently suggested as useful pigments. The manufacture and further particulars respecting white-lead are described under that heading and that of Lead (Compounds). Tests have proved that a paint made with 50 per cent. barytes and 50 per cent. white-lead is more durable as a pigment than pure white-lead paint.

Aluminium paint, now extensively employed for giving visibility to lamp and electric standards and other obstacles to safe motoring, as also for decorative purposes, can likewise be used in respect of creosoted

wood guard rails and fences, provided the proper vehicle is used and the wood is first allowed to dry for a time after treatment. It is also useful as a primer under house paints for wood. The mixing of so-called aluminium paints, made from powdered aluminium and mediums such as tung oil or turpentine or spirit, is the subject of a brochure issued by the British Aluminium Co., Ltd., of Adelaide House, London.

The term **pigments** is in practice applied chiefly to the insoluble mineral colouring matters or blacks incorporated in paints as distinct from organic colouring matters such as dyes and stains, which may be soluble in the vehicles used. Many of them, such as carbon, iron oxides of various colours, red-lead, sienna, ultramarine, umber, vermilion, etc., are described under their respective names. Titanium oxide pigments are more particularly referred to under that heading. Pigments have to be ground to a good commercial quality, 200-mesh being an effective size.

Lake pigments consisting of combinations of coal-tar dyes precipitated on inert bases such as clay, barytes, and whiting have also come largely into use of late for internal decorations.

Bituminous paints, prepared by dissolving bituminous substances in a suitable solvent (according to the application), with or without oils, resins, fillers, etc., are of special importance for many applications, as they can be easily applied in quick-drying and other solvents, of any thickness, are very adhesive, exhibit great preservative qualities and resistance to weather influences, acids, and alkalis; while their elasticity obviates cracking on iron and steel work.

It is inadvisable to use red oxide (ferric oxide) paint on chemical work where there is liability to attack by corrosive vapours; paints containing linseed oil are also better avoided, preference being given to bituminous paints or others made with mineral black and an entirely volatile solvent.

Lead aluminate prepared from litharge and alumina is said to form a white pigment unaffected by hydrogen sulphide, resistant to dilute acids, and possessing a covering power equal to that of white-lead. Zinc oxide or zinc sulphide pigments do not discolour in the presence of hydrogen sulphide gas, because the sulphide is white.

Graphite in paints into which it can be introduced acts as a preventive of water penetration. Silicon esters (see same) are used either alone or incorporated in other paints.

Linseed oil boiled, air-blown, or heat-bodied takes precedence of all other oils, although tung oil after heat treatment, as also perilla oil, admits of use, and even fish oils, such as menhaden oil, find, with others, a more or less limited application. Inhibition of drying of linseed oil paints is caused by tar paints.

A luminous paint of soft greenish glow and great durability is prepared by incorporating a small proportion of radium or mesothorium salt in a zinc sulphide base (particularly the native sulphide *wurtzite*, which is very responsive to the alpha-rays of radium disintegration), using some good binding material such as nitrocellulose lacquer. Highly luminous mixtures used in paints and enamels are obtained by

heating alkaline earths with certain proportions of sulphur, starch, lithium carbonate and traces of bismuth nitrate, rubidium nitrate, lead acetate, or other metallic salts.

**Liquid Portion** — Volatile liquids, such as benzene, petrol, rosin spirit, turpentine, naphtha, and acetone, are used in paint-making as thinners or vehicles, and upon evaporation leave the boiled linseed oil and mineral base on the coated surfaces. The linseed oil or substitute absorbs oxygen from the air, and mixed with the base forms a conglomerate solid mass constituting the real paint. Turpentine differs from the other vehicles named, inasmuch as it does not volatilize so quickly, and absorbing oxygen from the air (particularly in warm weather and sunlight), forms a skin of oxidized product, thus adding slightly to the weight of the dry paint.

**Driers** — See Varnishes.

**Titanium Oxide Paints** — See Titanium Compounds.

**Lead Titanate** is of high degree of chemical stability, has high opacity in oil vehicles, exerts a protective action on organic films, is resistant to chalking, and is inert in practically all types of vehicles. The colour is pale yellow, and density 7.3. See article by D. W. Robertson (*Ind. Eng. Chem.*, 28, 216 (1936)).

**White-lead Paint** — See White-Lead, and Lead Compounds.

**Enamel paints** are those ready mixed with varnish, so that upon drying they leave an enamelled face or gloss.

**Lithopone** is a white paint pigment and filling, largely used in the rubber and linoleum industries, having zinc sulphide, zinc oxide, and barium sulphate as chief basic constituents, prepared by strongly heating a mixture of zinc sulphide and barium sulphate, or one of barium sulphide and zinc sulphate, to redness. X-ray analysis has shown it to be a single mechanical mixture usually containing 27 to 28 per cent.  $\text{ZnS}$ , 70 to 71 per cent.  $\text{BaSO}_4$ , with 1 to  $1\frac{1}{2}$  per cent.  $\text{ZnO}$ .

**"Orr's Zinc White"** is made from a pigment mixture of about 70 to 72 per cent. barium sulphate and 28 to 30 per cent. zinc sulphide, prepared by the double decomposition of barium and zinc salts and some subsequent treatment. It exhibits good lustre and lasting qualities, and is not very susceptible to attack by hydrogen sulphide.

The precipitated compound of zinc sulphide and barium sulphate as prepared from solutions of zinc sulphate and barium sulphide in water has but little covering power, but after being heated to redness and plunged into water, ground, washed, and dried, it forms a satisfactory and durable pigment. It has a sp. gr. of about 4.25 and oil absorption 8 per cent., and is said to be the most opaque of all white pigments. A mixture of 95 per cent. with 5 per cent. of cadmium lithopone gives a nice cream-yellow product when rubbed out with oil.

The darkening of lithopone in some cases is due to the presence of contaminating metals which form dark-coloured sulphur compounds, particularly those which are susceptible to double decomposition with the light-sensitive zinc sulphide (lead, thallium, and manganese in particular, while iron, nickel, and cobalt alone are not so objectionable). Small percentages of certain salts are often incorporated to obviate this

darkening, trisodium phosphate being, perhaps, the best. In other cases the conclusion has been reached that darkening is due to reduction to metallic zinc and probably free sulphur on exposure to light, and that the re-whitening effect experienced in the dark is due to the oxidation of the free zinc.

**Cadmium lithopone** is a pigment mixture, in which the zinc of the ordinary product is replaced by cadmium and is valued on account of its rich yellow colour. (See "Albith".)

**"Sulfozone"** is a white pigment analogous to lithopone in which barium sulphate is replaced by calcium carbonate made by precipitation of a solution of calcium sulphide with one of zinc sulphate. It is said to be superior to lithopone in covering power and behaviour on drying.

**Casein Paints** — See Casein.

**Distemper** paints are compounded of bases with water and adhesives used as binders, such as size, glue, casein, etc.; casein distempers very quickly lose their adhesiveness, and should be used quickly after preparation. Antiseptics can be usefully incorporated in many distempers.

**"Tempera"** paints are made either from media containing egg-yolk or others consisting essentially of emulsions of oil and water, using casein, gum, or soap as emulsifying agents.

**Antifouling Compositions** are used for preventing the corrosion of the bottoms of iron ships and the adhesion of marine zoöphytes. The paint should be waterproof, so as to exclude water from contact with the iron, and the antifouling mixture placed on top of the paint should remain entirely undisturbable. Both have to be of a quick-drying character, hence they must be of a nature that dries quickly by loss of solvent as distinct from drying by oxidation, as oil varnishes do.

For waterline protection, zinc oxide in a slightly thickened linseed oil has been found satisfactory. Copper naphthenate, it is stated, forms an excellent base for paint used to protect the hulls of ships.

Iron oxide is a common pigment that is used with or without some kind of "filler," thinned down with naphtha, but the most satisfactory products are stated to be certain pitches and asphalt solutions, with or without a little linseed oil, using iron oxide as the pigment, and tar oil as the solvent or thinning material. All kinds of gums, as well as ordinary resin, are also used in compounding more or less satisfactory varnishes for use in connection with these paints.

Of the substances incorporated to render the composition **toxic** to marine life, compounds of copper and mercury rank first, including cuprous oxide, emerald green, and copper carbonate, and mercury in the form of oxide, sulphide, or, better still, mercury compounds of an organic character, such as mercury dinaphthyl. Ships' bottoms, adequately protected, can be kept in a reasonably good condition for from nine to twelve months.

**Aluminium stearate** has found increasing use in recent years in the paint trade to increase the body and to inhibit the settling of pigments. At ordinary temperatures it is practically insoluble, but dissolves readily

in hot mineral hydrocarbons, turpentine, benzol, etc., to form sols which gelate to various degrees upon cooling.

**Paint Remover** — Solvents, such as acetone, methanol, turpentine, and benzol, act as softeners of old paint, and, therefore, are useful as paint removers.

**References :** "Accelerated Weathering of Paints and Varnishes," by V. G. Jolly (*Chem. and Ind.*, **52**, 264 (1933)); "Antifouling Paints," by G. H. Young and others (*Ind. Eng. Chem.*, **36**, 341 (1944)); *Blacks and Pitches*, by H. M. Langton (E. Benn, Ltd., London); *The Manufacture of Paint*, by J. Cruickshank Smith (Scott, Greenwood and Son, London); *Outlines of Paint Technology*, by N. Heaton (C. Griffin and Co.); *Solvents and Thinners in the Paint and Varnish Industries*, by N. Heaton (E. Benn, Ltd., London); *The Technology of Paint and Varnish*, by A. H. Sabin (Chapman and Hall, London); *Physical and Chemical Examination of Paints, Varnishes, Lacquers, and Colors*, by Henry A. Gardner (Institute of Paint and Varnish Research, Washington); section on "Paints, Pigments, Varnishes, Resins, and Solvents," by Members of The Oil and Colour Chemists' Association in *Annual Reports of the Progress of Applied Chemistry* (Society of Chemical Industry); Colours, Driers, Gums and Resins, Lacquers, Siccatives, and Varnishes.

**"PALAU"** — An alloy of 80 per cent. gold, 20 per cent. palladium, used as a substitute for platinum.

**PALLADIUM (Pd) and its Compounds** — Atomic weight, 106.7. See Elements for other data. Palladium is a rare metal of the platinum group of elements, and is found associated in platinum ores to the extent of from  $\frac{1}{2}$  to 1 per cent., the chief source being *ouro poudre*, a native alloy with gold occurring in some Brazilian mines.

The metal can be obtained by ignition of the double palladium ammonium chloride, and is used as an alloy with gold, silver, or copper in dentistry, also for balance wheels of watches and as a catalyst, etc. The plating of white gold and silver renders them non-tarnishable.

Palladium is white, fairly ductile and malleable, and is especially interesting on account of its capability (particularly in the spongy condition) of "occluding" gases, including hydrogen, argon, neon, etc. If, for example, a wire of palladium be made the negative pole of a voltaic cell, it will in course of the decomposition of water absorb as much as 936 times its own volume of hydrogen gas, during which time it increases very largely in bulk. A piece of foil of the metal will, when heated to between 90° and 97° C. in an atmosphere of hydrogen, absorb as much as 643 times its own volume of that gas. Graham regarded hydrogen as a metallic element, and struck a special medal of an alloy with palladium stated to contain 900 volumes of hydrogen. Palladium is readily soluble in hot nitric acid.

Palladium forms alloys with many metals and is the chief rival of platinum in alloys for dentistry, jewellery, and catalysis. See *Rarer Metals*, by J. DeMent and H. C. Dake (Chemical Publishing Co., Brooklyn, N. Y.).

Palladium compounds resemble those of platinum in form and general characters. These include three **oxides**, namely, the dioxide ( $\text{PdO}_2$ ), the monoxide ( $\text{PdO}$ ), and the suboxide ( $\text{Pd}_2\text{O}$ ), all of which are easily transformed into metallic palladium upon heating; and the **chloride** ( $\text{PdCl}_2 \cdot 2\text{H}_2\text{O}$ ), **bromide** ( $\text{PdBr}_2$ ), **iodide** ( $\text{PdI}_2$ ), **nitrate** ( $\text{Pd}(\text{NO}_3)_2$ ), and **sulphate** ( $\text{PdSO}_4 \cdot 2\text{H}_2\text{O}$ ). The chloride is soluble in water and used in making indelible ink and photographing on porcelain, etc.

“**PALLAS**” — An alloy of palladium, platinum, and gold, described as harder, cheaper, and lighter than platinum; used as a substitute for platinum in making crucibles, etc.

**PALM OIL (Palm Butter)** is chiefly obtained from the West African oil palm *Elæis guineensis* and other species, including *Cocos butyracea* and *Avoira elæis*, which grow in abundance in Sierra Leone, Lagos, Gold Coast areas, and Senegal. Nigeria furnishes the principal supplies, with smaller amounts being obtained from *Elæis melanococca* in South America. The red palm oil of commerce comes from the pulp surrounding the kernels, and consists chiefly of the glycerides of palmitic and oleic acids, together with proportions of those of stearic and other acids and a large proportion of free palmitic acid, varying, it is stated, from 12 per cent. in the fresh to over 50 per cent. in old oil.

Palm oils, according to Hilditch and Jones, “closely resemble the tallows in their fundamental mode of assemblage” as regards glyceride structure.

The oil is best removed by pressure, solvents being subsequently applied. The oil is purified by melting to remove water or refined with lye, and can be decolorized by chemical agencies. One method of bleaching consists of immersing a screen of very fine mesh wire cloth in a bath of the oil and heating to  $100^\circ \text{C}$ ., the bleaching being attributed to the atmospheric oxygen adhering to the wire. It can also be bleached to some extent by means of fuller’s earth or “Frankonite.”

Fuel briquettes are made from the waste fibre and the shells of the *Elæis guineensis*. From the Nigerian palmeries, out of a total of 21 per cent. oil, only from 8 to 11 per cent. is obtained by the native methods of extraction.

The sp. gr. of the West African supply is generally given as 0.92 to 0.93, the i.v. as 13.5, and the ref. ind. as 1.4510 at  $60^\circ \text{C}$ . According to one account, the following are the constants of the two supplies above referred to:

		West African Palm Oil	South American Noli Palm Oil
Specific gravity	.. ..	0.8586	0.8636
Solidification point	.. ..	$36^\circ\text{--}46^\circ \text{C}$ .	$33.6^\circ \text{C}$ .
Saponification value	.. ..	196-205	199
Iodine value	.. ..	53-57	83.5

Palm oil varies in colour from orange-yellow to dark dirty red; it contains the fat-soluble vitamin A, and has a consistence varying from

that of butter to that of tallow, varieties being known as soft, hard, and mixed oils, according to the originating districts. It is subject to enzymic hydrolysis during storage, and is extensively and variously used in making margarine, soap, and candles, as a lubricant, also in the tin-plate industry, and (in admixture with tallow and some proportion of alkali) as railway-waggon grease.

The fruit is stated to yield approximately 37·5 per cent. pulp and 62·5 per cent. seeds, the 37·5 per cent. pulp being made up of 32·8 per cent. of palm oil, the remaining 4·7 per cent. being water and waste fibre; while the 62·5 per cent. seeds consist of 47·92 per cent. shells and 14·58 per cent. kernels, which contain about 50 per cent. of fat. The fleshy part of the fruit contains about 58 to 66 per cent. oil. The kernels of the West African oil palm contain about 50 per cent. of white fatty oil; those of the East African palms and of the South American fruit contain about 29 per cent. of oil, equal to 31·5 per cent. in the desiccated fruit.

Palm oil from the Belgian Congo is reported by Jamieson and McKinney as having sp. gr. 0·9146 at 25°/25° C.; ref. ind. 1·4578 at 40° C.; acid v. 20·6; sap. v. 197·9; i.v. (Hanus) 53·7, etc.; and percentages of the different glycerides present as: oleic 47·2; linolic 5·6; myristic 0·5; palmitic 40·8; stearic 5·2; and lignoceric 0·1. It is reported that among French West African oil palms one specimen gave 73·6 per cent. pulp in the fruit, 53·3 per cent. oil from the pulp by ether extraction, and 40·8 per cent. fat from the whole fruit by ether extraction. The African oil palm of the Gold Coast yields 77 to 80 per cent. oil calculated on the dry pulp, whereas the same species grown in Ceylon only gives about 66 to 69 per cent.

The crude **palm-nut** or kernel oil is yellowish, fat, and edible, and is obtained by crushing and pressing the kernels or extracting the oil from the crushed material by solvents. It consists of the glycerides of palmitic, stearic, oleic, myristic, lauric, caprylic, capric, and linoleic acids; is practically devoid of free fatty acids, and is soluble in alcohol, carbon disulphide, and ether. E. F. Armstrong (with others) gives the composition of the fatty acids from palm-kernel oil as follows: lauric acid, 52 per cent.; oleic acid, 16 per cent.; myristic acid, 15 per cent.; palmitic acid, 7·5 per cent.; caprylic acid, 3 per cent.; capric acid, 3 per cent.; stearic acid, 2·5 per cent.; and linoleic acid, 1 per cent. Hilditch and Jones give the characteristics of certain palm-nut oils studied by them as sap. v. varying from 280·2 to 283·8; i.v. ranging from 52·7 to 57·3; ref. ind., 1·450 to 1·452 at 60° C.

The kernels of the South American fruit contain 45·4 per cent. oil (equal to 48·7 per cent. in the desiccated seeds), used in soap-making, chocolate articles, and in pharmacy. The dry kernels of Curua palm oil (*Attalea spectabilis*) from Brazil yield 65·3 per cent. of semi-solid, greenish oil of sp. gr. 0·8693; m.p. 23·6° C.; sap. v., 259·5; i.v., 8·9; and ref. ind., 1·447. Guere palm nuts from Colombia, from a species of *Astrocaryum* (*A. Tucuma*, Mart.), have yielded 37·6 per cent. pale cream fat, m.p. 35·5° C.; sp. gr. 0·864 at 100°/15° C.; sap. v., 349·6; and i.v., 9·4.

Palm-kernel cake is a useful cattle foodstuff, and contains usually about 16 per cent. protein.

The oil-palm fibre may be employed in competition with the finer counts of flax, etc., for manufacturing purposes.

**PALM WAX** — See Waxes.

**PALMAROSA OIL** — See Geranium (Turkish) Oil.

**PALMETTO** — A tannin material (yield 25 per cent.) from the *Sabal serrulata* (the American palmetto palm) of Florida and Georgia.

**PALMITIC ACID** ( $C_{15}H_{31}.COOH$ ) — A member of the normal fatty acid series and a constituent of most of the harder fats, including spermaceti, and especially palm oils. It is tasteless, odourless, soluble in hot alcohol and ether, and is obtained in crystals of m.p.  $63^{\circ}C$ . Can be distilled at reduced pressure without change (vapour pressure at  $271^{\circ}C$ . is 100 mm.), and when saponified with alkalis forms hard soaps. (See Fats.)

**PALMITIN (TRIPALMITIN)** ( $C_3H_5(OOCC_{15}H_{31})_3$ ) — A white crystalline ester, of melting point  $60^{\circ}C$ ., occurring to a large extent in many vegetable oils, such as palm oil.

**"PALUDRINE"** — See Chlorguanide.

**PAMAQUIN ("Plasmochin")** ( $C_{42}H_{45}O_7N_3$ ) — An orange-yellow, odourless powder, namely, the 6-methoxy-8( $\omega$ -diethylamino- $\alpha$ -methylbutyl)-aminoquinoline salt of 2,2'-dihydroxy-1,1'-dinaphthylmethane-3,3'-dicarboxylic acid; insoluble in water; soluble in acetone containing 5 per cent. of water. It was introduced in 1924 as the first synthetic compound to show promise as an antimalarial agent to replace quinine. Pamaquin has a restricted action against the malarial parasite, exerting its effect chiefly on the gametocytes. It is used in conjunction with quinine or mepacrine. (See Mepacrine Hydrochloride.)

**PANCREATIC JUICE** — A secretion of alkaline reaction, containing pancreatine and other enzymes which assist in completing the digestion of substances in the chyme and emulsifying fatty bodies also present therein. When agitated with neutral oils, pancreatic juice makes perfect emulsions, and this emulsification enables the fatty matters to pass through the pores of the mucous membranes into the chyle ducts. In common with saliva it also has the property of converting starch into sugar. (See Enzymes, and pH Value.)

**PANCREATINE** — See Enzymes, and Pancreatic Juice.

**"PANDERMITE"** ( $3CaO,4BO_3,6H_2O$ ) — A trade name for mineral amorphous calcium borate (sp. gr., 2.26) or colemanite; used in compounding ceramic frits; its composition has also been represented as  $Ca_2B_6O_{11},5H_2O$ .

**PANTOTHENIC ACID** — See Vitamins.

**PAPAIN** — See Enzymes.

**PAPAVERINE** — See Opium.

**PAPAVERINE HYDROCHLORIDE** ( $C_{20}H_{21}O_4N, HCl$ ) — A white crystalline solid, soluble in water, alcohol, and chloroform; insoluble in ether; m.p.  $215^{\circ}$  to  $225^{\circ}$  C. It is used in medicine as an antispasmodic in the treatment of hypertension due to arterial spasm.

**PAPER** may be described as a fabric made by the deposition of finely divided fibres from a state of suspension in water by means of a sieve or strainer, followed by rolling and calendering. There are many varieties, including those made for newspapers and ordinary printing, writing papers, wrapping and packing papers, and a great number of miscellaneous characters. The paper is spun by spreading the pulp mixture over a wire cloth, thus forming a continuous sheet, which is afterwards pressed between hot rollers, thus drying and at the same time polishing it. Over 90 per cent. of the world's paper is now made from wood cellulose in varying states of purity.

It was made almost exclusively from rags down to 1866, but in that year esparto grass was first employed, and since then cotton, flax, hemp, rhea (ramie), jute, linden bast, adonsonia bast, sisal hemp, yucca, hibiscus, New Zealand flax, aloe, common nettle, phormium, broom, caroa fibre, paper mulberry, straws, and wood pulp have been very extensively used in its manufacture, as also the cellulose made from the bamboo and Savannah grasses; in point of fact, any fibrous vegetable matter can be turned into paper if properly treated, although grasses are not so tractable.

Chemically pure rag paper is generally supposed to be the best for use in respect of documents calling for the greatest preservation, and *Colombian Pita*, a fibre of great strength and durability, gives a paper said to be unequalled by any other material. While it is generally understood that the best grades are those made from cotton and flax, by reason of certain physical properties enabling close interlocking of their fibres and thus promoting resistance to handling, that made from esparto grass has better durability than paper made from chemical wood. The acid ("sulphite") process fails to remove certain adventitious deleterious constituents associated with the cellulose, while the alkaline process produces a pulp possessing a better degree of permanence. These processes are described later.

Cellulose is not present in the free state in plants, but is in admixture or combination with other groups, such as lignin, fats, waxes, etc.

"**Mechanical pulp**" consists chiefly of ligno-cellulose, and no attempt is made to remove the resinous and other associated substances. It is produced by cutting up the logs of wood into certain lengths (after removal of the bark) and grinding in water in a longitudinal direction under pressure by a rotary grindstone. The product is then strained and made up into sheets by passing it over a rotary wire mesh, partially dried and pressed by a rolling process. This mechanical pulp used i. admixture with from 20 to 60 per cent. of "sulphite" pulp is used for the cheaper qualities of printing papers and news-print. Decolorizing this pulp by the use of sodium peroxide is discussed in *Chemical and Engineering News*, 22, 332 (1944).

In the "**soda process**" of preparing cellulose for paper-making from wood, spruce, pine, larch, birch, and poplar (which vary in their constituent proportions of cellulose and lignin) are employed with or without the incorporation of rag pulp. To prepare the wood pulp the bark is removed, and after cutting up into small pieces or chips, the wood is heated in a strong solution of caustic soda under some pressure, in which process the lignin and other associated bodies are dissolved and the cellulose remains undissolved. The pulp amounts to about one-third of the original weight of the wood, and after washing to free it from associated soda the pulp is ready for bleaching.

In the "**sulphite process**" (by which the greater bulk of the world's paper is produced) the chipped wood is boiled under pressure of from 50 to 100 pounds per square inch in a solution of calcium bisulphite ( $\text{Ca}(\text{HSO}_3)_2$ ) and sulphurous acid ( $\text{H}_2\text{SO}_3$ ), made by passing a current of sulphur dioxide through milk of lime or subjecting wetted limestone to the action of sulphur dioxide. This digestion renders the non-cellulose parts soluble, the yield of cellulose being influenced by the temperature (varying from 125° to 155° C.) and other factors. In general 48 to 55 per cent. of the wood is obtained as cellulose of good enough character to use for paper-making. (See *Chemistry of Pulp and Paper-Making*, by E. Sutermeister (John Wiley and Sons, New York); *Modern Pulp and Paper Making*, by G. S. Witham, Sr. (Reinhold Publishing Corp., New York); *The Chemistry of Cellulose and Wood*, by A. W. Schorger (McGraw-Hill Book Co., New York); *The Manufacture of Pulp and Paper*, by the Joint Executive Committee on Vocational Education Representing the Pulp and Paper Industry of the United States and Canada (McGraw-Hill Book Co., New York), Volumes 4 and 5.)

"**Kraft Process**" — When chipped wood is cooked with a mixture of caustic soda and sodium sulphide under pressure the resulting pulp can be made into paper of very high strength. It is used in making sacks for carrying plaster, cement, etc., and for wrapping.

The **bleaching** of pulp is effected by the use of either bleaching-powder solution, sodium hypochlorite, or sulphur dioxide, and when chlorinating preparations are used, any excess of chlorine is removed by the use of an "antichlor," such as sodium thiosulphate, before the sizing operation.

**Sizing and Loading** — When the pulp, after washing, has been sufficiently beaten in order to separate the individual fibres, size is added to give the paper water or ink resisting qualities, mineral matter added to load up the pores of the paper, and colouring matter if desired. The mineral matters so used include china clay, talc, chalk, witherite, and calcium sulphate; while umber, ochre, and red oxide are among the colouring materials employed. Sizing, when required, is effected either by adding resin or sodium resinate to the pulp, and afterwards adding alum solution or dilute sulphuric acid so as to fix it in the body of the paper; or the spun paper is passed through a bath of gelatine solution and then through one of alum solution to precipitate the gelatine in the pores of the paper. Or instead of using resin for sizing, K.C.E.— 26

soap solutions can be used, particularly the alkali salts of stearic acid, alone or in conjunction with sodium silicate, alum being used as the precipitant. Sodium silicate alone or with starch is also used, and it helps to retain and cement short fibres in the sheet. So-called "colloidal resin," for use in sizing paper pulp, is prepared by dissolving it in alcohol, and then diluting the solution with water, so making an emulsion, which becomes an effective sizing material when subsequently coagulated by the addition of aluminium sulphate.

The published analysis of an English clay used as a filler is as follows : Silica, 45.92 per cent. ; alumina, 38.43 per cent. ; ferric oxide, 0.71 per cent. ; lime, 1.18 per cent. ; magnesia, 0.21 per cent. ; alkalis ( $K_2O$ ), 0.78 per cent. ; total water, 12.77 per cent.

The **dyeing** of paper is carried out by precipitating the colouring matter directly on to the prepared pulp or indirectly by dissolving it in boiling water to which a little ammonium hydroxide or acetic acid is added (according to the nature of the dyestuff) and mixing with the pulp in the beating machine.

There is an electrical process for preparing pulp from broken wood by exposing it in a bath of sodium chloride to a current of chlorine at  $126^{\circ}C$ . ; hypochlorous acid and caustic soda thus produced acting collectively ; and a chlorine process is based upon the method advocated by Cross and Bevan for preparing cellulose free from lignin. (See Cellulose.)

The **sulphite liquor** resulting from paper-making can be utilized for alcohol manufacture, also for the preparation of a useful adhesive, and from the soda liquor an activated carbon can be made by incineration of the by-product following upon the recovery of the soda. It is also used for road-watering, thus binding dust and making the track smooth and solid.

A process for the use of asphalt mixed with clay and water is used for strengthening and waterproofing heavy papers and boards, the mixture being intercalated between layers of the prepared pulp.

The addition of rubber latex to paper pulp gives the resulting paper remarkable strength and waterproof character, and it does not crack upon folding.

Parchment paper is produced by dipping paper into sulphuric acid of about 50 per cent. strength, whereby it is partially hydrated and gelatinized, after which it is washed free from the acid and carefully dried.

Papier-mâché consists of mashed or pulp paper pasted together, sometimes mixed with other substances, which admits of varnishing or lacquering or inlaying with mother-of-pearl, etc.

Transparent paper is made from viscose.

The **de-inking** of paper is carried out by the use of strong alkaline solutions to dissolve the varnish and set free the carbon, which is subsequently removed by the use of some finely divided colloidal agent of the nature of clay or talc. The natural clay known as bentonite is said to be an efficient agent of this class, being of detergent character.

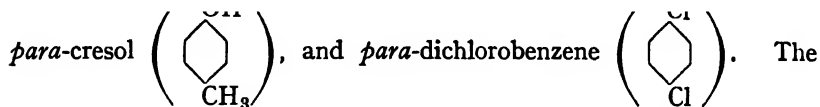
*References : A Textbook of Paper Making, by Cross and Bevan*

(E. and F. Spon, London); *The Digestion of Grasses and Bamboo for Paper-Making*, by W. Raitt (Crosby Lockwood and Son, London); *Practical Paper-Making*, by R. H. Clapperton (Crosby Lockwood and Son, London); "Cellophane," Cellulose, Millboard, Silk Substitutes, Wood, and Wool.

**PAPYRUS** — Name of a genus of aquatic sedge plants of the N.O. Cyperaceæ, from the pith of which the paper of the Egyptians was made.

**PARA-AMINOPHENOL** — See Aminophenols.

**PARA COMPOUNDS** are substitution products derived from benzene in which the substituting radicals or groups are constitutionally situated in certain definite *opposite* positions on the nucleus, for example,



positions are now more commonly expressed numerically, for example, 1,4-dichlorobenzene for the latter substance, and 4-methylphenol for the former. (See Benzene Ring.)

**PARACHOR** — The fourth root of the surface tension of a liquid is proportional to the difference between the density of a liquid and the density of its vapour, and the proportionality constant is only slightly affected by change of temperature (up to temperatures approximately 30° C. below the critical temperature of the substance). This may be represented thus:  $\gamma^{\frac{1}{4}} = K(D-d)$ , where  $\gamma$  = surface tension;  $D$  = density of the liquid;  $d$  = density of the vapour; and  $K$  = proportionality constant. This result was announced by D. B. MacLeod, in 1923.

In the following year, S. Sugden proposed that the ratio  $\frac{\gamma^{\frac{1}{4}}}{D-d}$ , multiplied by the molecular weight,  $M$ , of the substance be termed the *parachor*, which turns out to be close to an additive property of substances. Some of the Sugden parachor values are :

Carbon .. ..	4.8	Olefin double bond .. ..	23.2
Hydrogen .. ..	17.1		
Oxygen .. ..	20.0	Acetylene triple bond .. ..	46.6
Nitrogen .. ..	12.5	5-Membered ring (cyclopentane derivatives) .. ..	8.5
Sulphur .. ..	48.2		
Chlorine .. ..	54.3	6-Membered ring (cyclohexane derivatives) .. ..	6.1
Bromine .. ..	68.0		
Iodine .. ..	91.0		

As an example, suppose it is assumed that benzene ( $\text{C}_6\text{H}_6$ ) has three double bonds and three single bonds in a  $\text{C}_6$ -ring, what is its parachor?

Assumption	Parachor Component	Parachor of Benzene
6 Carbon atoms .. ..	$6 \times 4.8$	28.8
6 Hydrogen atoms .. ..	$6 \times 17.1$	102.6
6-Membered ring .. ..	$1 \times 6.1$	6.1
3 Double bonds .. ..	$3 \times 23.2$	69.6
Summation of above assumptions		207.1
Experimentally determined value		206.2

*References*: J. Reilly and W. N. Rae, *Physico-chemical Methods* (D. Van Nostrand Co., New York); A. Weissberger, *Physical Methods of Organic Chemistry* (Interscience Publishers, New York); S. Sugden, *The Parachor and Valency* (G. Routledge and Sons, London); T. W. Gibling, *J. Chem. Soc.*, 1941, 299; 1942, 661; 1943, 146; R. Samuel, *J. Chem. Physics*, 12, 157 (1944).

**PARA-COUMARONE RESIN** — See Coumarone Resin.

**PARA-CRESOL** — See Cresol.

**PARA-NITRANILINE** — An intermediate. (See Nitranilines.)

**PARA-NITROPHENOL** — See Nitrophenol.

**PARA-PHENYLENEDIAMINE** ( $C_6H_4(NH_2)_2$ ) (1, 4) — A colourless crystalline intermediate, soluble in water, alcohol, and ether, of m.p. 140° C. and b.p. 267° C.

**PARADISE, GRAINS OF** — See Grains of Paradise.

**PARAFFIN OIL** — A general name given to a number of hydrocarbons heavier than kerosene, of flash-point from 300° to 450° F., variously derived from the distillation of wood, coal, lignite, peat, shale, petroleum, etc. There are varieties of yellowish, brown, red, or green colour, used for lubricating purposes and in leather-dressing, etc., a refined quality of high-boiling character prepared from petroleum being used in medicine. (See "Nujol," Petroleum, and "Vaseline".)

**PARAFFIN WAX** — See Waxes.

**PARAFFINS** — See Hydrocarbons, and Petroleum.

**PARAFFINUM LIQUIDUM, B.P. (Liquid Paraffin)** — A colourless, viscous oily liquid being a mixture of hydrocarbons obtained from petroleum. The *British Pharmacopæia* (1948) specifies its weight per millilitre at 20° C. as 0.865 to 0.890 gram. It is used in medicine as an internal lubricant for the treatment of constipation.

**PARAFFINUM LIQUIDUM LEVE (Light Liquid Paraffin)** — A colourless oily liquid, being a mixture of hydrocarbons obtained from petroleum. The *British Pharmacopæia* (1948) specifies its weight per millilitre at 20° C. as 0.830 to 0.870 gram. It is used in pharmaceutical preparations for oily spray solutions containing menthol, thymol, volatile oils, etc.

**PARAFORMALDEHYDE (Paraform)** — A white solid polymer of formaldehyde  $(\text{CH}_2\text{O})_n$ ; insoluble in water, soluble in hot water with depolymerization. On vaporization, it is depolymerized into formaldehyde and is used for disinfection by fumigation. (See Formaldehyde, and Fumigation.)

**PARALDEHYDE or PARA-ALDEHYDE**  $((\text{C}_2\text{H}_4\text{O})_3)$  — A water-white liquid of pleasant odour, being a polymer of acetaldehyde; used as an hypnotic; sp. gr. 0.994, and b.p.  $124^\circ\text{C}$ . The commercial product of sp. gr. 0.940 to 0.995 has a calorific value of about 6,000 calories, and may be used as a liquid fuel in place of denatured alcohol in lamps, etc. (See Aldehydes.)

**"PARATHION"** — A yellow liquid of b.p. approximately  $375^\circ\text{C}$ ., and sp. gr. 1.26, having the formula  $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{S})\text{OC}_6\text{H}_4\text{NO}_2$ , having powerful insecticidal properties, especially against aphids and mites. It is toxic to higher animals. (See article by Gleissner in *Agric. Chemicals*, Oct., 1947; also Insecticides, and Tetraethyl Pyrophosphate.)

**PARCHMENT** — Made from sheepskins by liming in order to kill the roots of the wool and to effect its easy removal by plucking, after which they are again limed, fleshed, and the fat removed by scraping, and subsequently split in order to separate the outer skin from the inner one, which, after some further treatment, ultimately becomes parchment. The outer skin, or "skiver" (as it is known), is tanned into light leather and used for bookbinding and lining hats and shoes. (See Paper.)

**PAREIRA ROOT** (*Chondodendron platyphyllum*), yields alkaloids, one of which is named isochondodendrine, of the composition  $\text{C}_{18}\text{H}_{19}\text{O}_3\text{N}$ . These alkaloids are different from those obtained from the bark of *Nactendra Rodiaei*, one of which is named isobebeerine.

**PARIS BLUE** — A blue compound obtained by heating aniline with tin chloride; used in ink, paint, and varnish making, and for dyeing.

**PARIS GREEN** — See Copper (Compounds).

**PARIS WHITE** — Brands of whiting.

**PARKER PROCESS for Rust-proofing** — See Rustless Iron and Steel.

**"PARMONE"** (Du Pont) — Trade-mark for a fruit-drop inhibitor based on *alpha*-naphthaleneacetic acid. Used to retard the dropping of apples and pears.

**PARSLEY OIL** — A colourless or yellowish-green volatile oil distilled from the fruit of *Carum Petroselinum* (Fam. Umbelliferæ); soluble in alcohol and ether; sp. gr. 1.040 to 1.100 at  $15^\circ\text{C}$ . It contains apiol together with terpenes.

**PARTICLES** — See *Symposium on New Methods for Particle Size Determination in the Subsieve Range*, 1941 (American Society for Testing Materials, Philadelphia); also Colloid Chemistry, Paints, and Ultra-Centrifuge.

For the charged particles concerned with radioactivity and internal atomic changes, see Nuclear Chemistry.

**"PARZATE"** (Du Pont) — Trade-mark for a fungicide based on zinc ethylene *bis*-dithiocarbamate. Used as powder or liquid for the control of early and late blight on potatoes, tomatoes, and celery, blue mould on tobacco, brown rot on peaches, and petal blight on azaleas.

**PASSIVITY** — When used as an anode in an electrolytic cell and with a potential more positive than the reversible value for the electrolyte, iron, cobalt, and nickel show a definite resistance to dissolving and to going into solution (polarization). In spite of this marked polarization, these metals when used as anodes will dissolve quantitatively in accordance with Faraday's law. However, if the current density is increased, then a point is soon reached at which the anode potential rises suddenly and there is a definite decrease in the flow of current. The metal of the anode nearly ceases to dissolve. The metal is said to be in the passive state. Chromium, molybdenum, and tungsten can also be rendered passive.

If iron is dipped into concentrated nitric acid the metal begins to dissolve and then quickly stops dissolving to assume an inertness much greater than would be expected. For example, the passive iron so produced will not displace silver from a solution of silver nitrate, nor copper from a solution of copper sulphate. The passivity can be removed, however, by simply scratching the surface or by merely touching the passive metal by a more active metal. Nitric acid causes nickel, cobalt, and chromium to become likewise passive.

Metals rendered passive by electrical and chemical methods look much the same as the ordinary metals. There is little doubt that the basic cause is the same in all cases of passive metals. Most theories explaining the passivity of metals are modifications of the theory put forward by Michael Faraday in 1836. He suggested the surface becomes passive because it is oxidized, although the layer may be so thin that it is invisible. This concept has been substantially verified.

See *Metallic Corrosion, Passivity and Protection*, by U. R. Evans (Longmans, Green and Co., London and New York); and *Corrosion*.

**PASTEURIZATION** — See Milk.

**PATAUÁ OIL** — Obtained from the fruit of the patauá palm tree of Brazil. The fruit yields about 10 per cent. of edible oil.

**PATCHOULI OIL** — A volatile oil obtained by distillation from the leaves of *Pogostemon Patchouli* (Fam. Labiatae), indigenous to Northern India and China and grown in the West Indies, Java, and the Straits Settlements. It is light brown in colour and contains a tertiary alcohol ( $C_{15}H_{26}O$ ), together with cadinene and cedrene, eugenol and cinnamic aldehyde; soluble in alcohol and ether; sp. gr. 0.950 to 0.995 at 15° C.; opt. rot.  $-50^{\circ}$  to  $-68^{\circ}$  at 20° C.; ref. ind. 1.504 to 1.520 at 20° C. Patchouli oil is used in perfumery.

**PATINA** — See Copper.

**PATRONITE** — The Minasagra deposit in the Junin Department of Peru, consisting of mixed hydrocarbons and vanadium sulphide, containing about 20 to 26 per cent. vanadium and about 60 per cent. sulphur, being the chief source of vanadium. (See Vanadium.)

**PEANUT OIL** — See *Arachis Oil*.

**PEARL ASH** — An American crude potassium carbonate prepared from wood ashes by concentrating the lixiviate until the less soluble salts have crystallized out, then evaporating the mother-liquor to dryness and calcining the residue. It is used in glass and soap making, etc.

**PEARLS** are secretions of certain shell-fishes such as the pearl oyster, having a sp. gr. of 2.5 to 2.75, and consist of calcium carbonate radially interstratified with certain membranes resulting from chemical changes, to a contamination of which the occasional loss of lustre is probably due. The chief fisheries are in the Persian Gulf, Ceylon, and Lower California.

When calcium carbonate is precipitated in the presence of gelatine in thin layers, a deposit of a nacreous (pearly) structure is obtained, which becomes opaque upon prolonged drying at 50° C., just as mother of pearl or pearl itself "dies," and this fact is supposed to support the accepted views as to the physical and chemical constitution of these substances. So-called artificial pearls have been produced by the Japanese by a method of artificial stimulation of the oyster, and this is to be regarded as a modification of the natural formation. But two French chemists (L. Clément and C. Rivière) have, it is stated, succeeded in synthesizing pearls by a purely chemical process as follows: a solution is made containing 80 parts water, 5 parts gelatine (in place of the albuminoid material contained in natural pearls), and 15 parts of a calcium salt, such as the lactate. After filtering hot, the object is coated with this solution and slowly submitted to the action of a precipitated solution containing sodium carbonate, trisodium phosphate, and gelatine, the gelatine being thus deposited as a very fine network; these conditions secure the required iridescence, layers of nacreous material being built up in concentric spheres, but not in radial form as in the natural pearl, which still remains unrivalled.

A so-called "pearl essence," consisting of brilliant crystalloids, can be prepared from the scales, swimming bladders, and other integuments of certain fish. (See *Mother of Pearl*.)

**PEAT** — A carbonaceous deposit widely distributed and occurring in fen and marshy areas, resulting from chemical changes affecting the mossy and other plants which abound therein, often found in beds of from some inches to many feet in thickness, and containing, when dry, from 24 to 30 per cent. of carbon. When air-dried, peat forms a valuable fuel, and when coked in ovens or distilled, it yields many valuable products allied in character to those derived from lignite and coal.

The percentage of water in peat, as it occurs in a drained bog, varies from 85 to 90, and this can be reduced by warming to the boiling-point of water or blowing steam through it and mechanical pressure to from 35 to 50 per cent. Using Somerset peat and cold pressure of nearly 800 pounds per square inch, the percentage is only reduced to about 75. The "ten Bosch process" for removing water from peat prior to its

conversion into briquettes is conducted by submitting it to steam at 140° to 160° C. under the necessary pressure, and then subjecting it to mechanical pressure, thus reducing the water content to about 25 per cent. Centrifuges have been tried for the extraction of water with incomplete success, the "Gee" centrifuge proving the best.

It is stated that by use of the so-called electro-osmose filter, 85 parts of water can be easily removed from hydraulically mined peat containing only 5 parts of the dry substance in 100 parts of suspension, so that where water-power is available to produce electricity sufficiently cheap, and peat beds are near enough and thick enough, this process of drying holds out promise. When the electric current is passed through the aqueous mass, the peat collects in a more or less dry state on the positive pole in a compact form.

F. M. Perkin prepared peat briquettes containing only 18 to 20 per cent. water by macerating the peat, extruding as much water as possible, then exposing the mass in an autoclave under pressure to produce a sudden rise of temperature and discharging suddenly. Some briquettes made from Argyllshire peat in this way had a sp. gr. of 1.29 and calorific value 8,558 B.Th.U., contained volatile matter 51.41 per cent., water 15.12 per cent., fixed carbon 31.97 per cent., mineral matter 2.50 per cent., nitrogen 2.66 per cent., and sulphur 0.27 per cent.

The average calorific value for Irish air-dried peat is about 6,850 B.Th.U. per lb., and its ash content is 3 per cent. The nitrogen content increases from the surface (1 per cent.) downwards (to 2.5 per cent. at the bottom of deep bogs), and it is calculated that it should yield about 100 pounds of ammonium sulphate per ton of air-dried peat. Its main uses, however, at present are as litter, cattle food, and fuel, the last named including the various distillation products. It also has value as a fertilizer by reason of its nitrogen content, the black decomposed qualities being best for such use, and it has been recommended as a useful material for softening boiler-feed water.

To be of use for carbonization, it is stated that peat must not contain more than 20 to 25 per cent. of moisture or 5 per cent. ash, and it then yields 30 per cent. gas, 5 per cent. tar, and 0.25 per cent. ammonia at a retort temperature of 1,100° C. A block of peat upon carbonization shrinks, but maintains its integrity fairly well to the end.

The incomplete combustion of peat in a gas-producer yields some proportion of volatile oils and wax (resembling the Montana wax of lignite), a soft pitch being left behind. The volatile oils contain a proportion of phenolic bodies of an acidic character allied to those yielded by the distillation of blast-furnace tar, that is to say, of a higher germicidal character than ordinary coal-tar distillates.

Wet peat from an undrained bog contains about 8 per cent. dry material and will yield 2.8 per cent. charcoal, while a well-drained bog gives a peat of which 100 tons will yield about 3.5 tons of charcoal. Coke from peat can be made soft or hard at will, harder, it is said, than coke-oven coke, and of sp. gr. from 0.75 to 1.4, some qualities being exceptionally valuable for iron-smelting and for hardening steel. It has been estimated that in Ireland the peat contained in the

bogs amounts to more than ten times the *proved* coal reserves of that country.

Humoceric acid ( $C_{10}H_{34}O_2$ ) is the name given to a colourless, crystalline body isolated from peat by Ossian Aschan. The lignin content of peat is stated to decrease with age, together with a corresponding increase in the humic acids content. (See Humus, and Dopplerite.)

It is possible to obtain alcohol from peat by a fermentation process, and the peat pulp can also be made into paper.

From investigations made, it is believed that in Ontario peat can be made commercially to compete with anthracite. Extensive investigations as to the utilization of North Dakota peat have been made and are reported in *Ind. Eng. Chem.*

*References* : Peat, peat drying, and peat utilization, World Power Conference in 1928 (*Chem. and Ind.*, 47, 1028 (1928)) ; D. Brownlie on "The Canadian Government Peat Report" (*Ind. Chem.*, 2, 355 (1926)).

**PECTINS and PECTIC SUBSTANCES** — These are complex colloidal carbohydrate derivatives which occur in, or are prepared from, plants. The pectins are polysaccharoses, closely related to the sugars, mucilages, and gums, and occur in many fruits such as apples, pears, and grapes, also in carrots, turnips, beans, many root organs, and the tissues of numerous plants including the seeds of oranges, grape fruit, etc., reaching their maximum during the process of ripening, and then diminishing as the fruit (apple, for instance) becomes over-ripe. The dried pulp of sugar-beet contains about 25 per cent. pectin.

The pectins are soluble bodies derived from pectose, an insoluble inter-cellular substance (possibly a derivative of cellulose), the conversion taking place during the ripening of fruit, instanced also in the retting of flax, and attributed to the direct action of an enzyme termed pectinase. By the action of another enzyme named pectase, the pectins are resolved into pectic acids, the calcium salts of which give fruit juices the property of jellifying. Pectic acids are also produced from pectins and pectose by boiling for some hours with dilute alkali solutions. Pectinogen is described as the methyl ester of pectic acid.

The different pectins are hydrolysed by boiling with dilute mineral acids into the saccharoid bodies, *d*-galactose and *l*-arabinose ; and by dilute sodium hydroxide, forming the sodium salt of pectic acid. Chemically, they probably consist of the dimethylisopropenyl esters of pectic acid. They appear to have a ring complex containing galacturonic acid ( $CHO(CHOH)_4COOH$ ), a compound which, when distilled with hydrochloric acid, breaks up into furfural ( $C_5H_4O_2$ ) and carbon dioxide:  $C_6H_{10}O_7 = C_5H_4O_2 + CO_2 + 3H_2O$ . The pectins are responsible for the formation of jelly in making jams and preserves, and apple pectin is used for thickening jam. The "Bloom Gelometer" is a device for measuring the jelly-strength of fruit jellies. (See Fellers and Griffiths, *B.C.A.*, B, 1928, 727.)

Pectin is precipitated as a jelly on boiling and by the action of acids. (See "Citrus Pectin," by A. G. Olsen (*Ind. Eng. Chem.*, 25, 699 (1933)) ; "The Chemistry and Physiology of the Pectins" (*Bot.* 26\*

*Rev.*, **12**, 535 (1946)); their nomenclature in *Chem. Eng. News*, **22**, 105 (1944); "Pectin Studies," by L. H. Lampitt *et al.* (*J. Soc. Chem. Ind.*, **56**, 270 T(1937); **58**, 29(1939); **66**, 121, 157 (1947); **67**, 101 (1948); **69**, 53 (1950)); *The Pectic Substances*, by Z. I. Kertesz (Interscience Publishers, New York); and Pectose.)

**PECTOGRAPHS** — Deposits from colloidal solutions produced by desiccation of sols.

**PECTOSE** — The pulpy part of fleshy unripe fruits, insoluble in water, and which becomes converted into pectin (which is soluble) by the agency of heat or by the ripening process. It is this last-named substance that imparts to their juices the property of gelatinizing (pectization) when boiled. Pectose is not of invariable composition, but has to be viewed as a compound of methoxylated pectin in which from 1 to 8 of the methoxy groups may be replaced by cellulose residues. (See Pectins.)

**PEDOLOGY** — The science of the soil. (See Agricultural Chemistry.)

"**PEDOX**" (Du Pont) — Trade-name for sodium perborate monohydrate ( $\text{NaBO}_3 \cdot \text{H}_2\text{O}$ ). Used for bleaching textiles, and as a constituent of dentifrices and washing powders.

**PELARGONIC ACID** ( $\text{C}_8\text{H}_{17}\text{COOH}$ ) — A product of the oxidation of oleic acid, and contained naturally in the volatile oil of *Pelargonium roseum*, N.O. Geraniaceæ, a native of the Cape of Good Hope and some other parts of South Africa. (See Geranium Oil.)

**PELIGOT BLUE** — Hydrated copper oxide, used as a pigment.

**PELLETIERINE TANNATE** — A light yellow, odourless, amorphous powder, consisting of a mixture of the tannates of the alkaloids obtained from the bark of the root and stem of *Punica Granatum*; sparingly soluble in water; soluble in alcohol. It has a specific action against the tape-worm and is used in medicine as a tænicide.

**PENAK RESIN** — See Gums and Resins.

**PENCILS** — See Inks.

**PENETROMETER** — A penetrating apparatus used for testing the consistency of asphalt, greases, etc.

**PENICILLIN** — An antibiotic substance produced when the mould *Penicillium notatum* and other related micro-organisms are grown under suitable conditions. It may be converted to the calcium, potassium, or sodium salt.

The original discovery of penicillin by Sir Alexander Fleming in 1929 resulted from the observation that a culture of the pathogenic organism *Staphylococcus aureus* ceased to grow in the presence of a mould subsequently identified as *Penicillium notatum*. Further development was

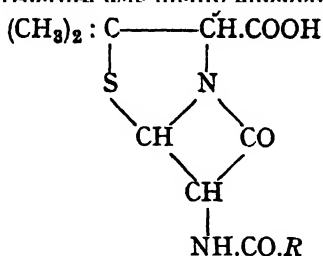
undertaken by Sir Howard Florey and Abraham, Chain, and Heatley in 1939, when sufficient material was prepared to enable chemical tests and preliminary clinical trials to be conducted. In 1941, owing to World War II, it was not possible to develop commercial production in Great Britain and, at the instigation of the Rockefeller Foundation, the British workers visited America to place at the disposal of American manufacturers the information gained from the preliminary experiments in Great Britain. As a result, the U.S. Northern Regional Research Laboratory at Peoria, Illinois, undertook the problem of producing sufficient penicillin for further clinical testing. From these investigations the method of submerged culture was developed and the production of penicillin enormously increased.

*Submerged Culture.* A suitable strain of the mould (*Penicillium notatum* N.R.R.L.832) is first cultivated in 400-gallon containers and transferred to 10,000-gallon fermenters. Fermentation is carried out at 23° to 24° C. and the time is determined by control assays of the penicillin content of the medium. The liquid medium used contains inorganic salts with 1 to 2 per cent. of lactose and 2 to 3 per cent. of corn-steep liquor. The broth and all vessels used must be previously sterilized, and during fermentation sterile air is passed through the culture in order to maintain aerobic conditions throughout the whole volume of the medium. When the penicillin content has reached its maximum, the broth is filtered and acidified with phosphoric acid. The penicillin, in the form of the acid, is extracted by means of organic solvents such as amyl acetate or chloroform, and after separation of the organic solution the penicillin is transferred to aqueous solution in the form of the sodium salt. The process is repeated by acidifying the aqueous solution, extracting with an organic solvent and re-conversion to the sodium salt. Since penicillin is destroyed by heat, the final aqueous solution is subjected to "freeze-drying," in which a frozen solution is subjected to high vacuum so that the ice sublimates, leaving a residue of dry sodium penicillin salt. The material produced by this method still contains some impurities and consists of a yellow or brown hygroscopic solid. Penicillin can be further purified by conversion to the hexamethylenediamine salt, washing out the impurities with an organic solvent such as amyl alcohol and subsequent re-conversion to the sodium salt or potassium salt. For an account of the manufacture of penicillin, see *Pharm. J.*, 1, 399 (1946). For methods of purification, see *British Patent Application*, Nos. 11255/45, 16212/45, and 11255/45.

*Surface Culture.* In this process, which has now been superseded by the submerged culture process, the strain of the organism used is *P. notatum* N.R.R.L.1249.B21. The mould is grown on the surface of a liquid medium contained in numerous small flasks. After fermentation the liquid medium is filtered and subjected to extraction processes similar to those described above. This method is now only of historical interest.

*Chemistry.* Penicillin is an organic acid having the molecular formula  $C_9H_{11}O_4N_2SR$ , several different penicillins having been identified and differing in the radical, *R*. The chemistry of penicillin

proved to be a difficult problem but after a number of unsuccessful attempts the structure was finally elucidated as follows:



$-\text{CH}_2 \cdot \text{CH}=\text{CH} \cdot \text{CH}_2 \cdot \text{CH}_3$	$\Delta^2$ -pentenyl	Penicillin-I or Penicillin F
$-\text{CH}_2 \cdot \text{C}_6\text{H}_5$	benzyl	Penicillin-II or Penicillin G
$-\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$	<i>p</i> -hydroxy-benzyl	Penicillin-III or Penicillin X
$-\text{CH}_2 \cdot (\text{CH}_2)_5 \cdot \text{CH}_3$	<i>n</i> -heptyl	Penicillin-IV or Penicillin K

When pure the sodium and potassium salts are white crystalline solids dissolving readily in water. The pure calcium salt is a white amorphous powder, very soluble in water but dissolving less readily than the sodium salt.

Penicillin-sodium of clinical purity is a yellow to brownish solid having a potency of not less than 900 units per milligram. Both the crystalline and clinical material available commercially consist mainly of Penicillin-II or Penicillin G.

For an account of the chemistry of Penicillin, see *Nature*, **156**, 766 (1945); *Science*, **102**, 627 (1945); and *Pharm. J.*, **1**, 76 (1946). See also *Science*, **106**, 653 (1947); **106**, 503 (1947); **106**, 192 (1947). The separation and characterization of some of the penicillins by the method of counter-current distribution is described by L. C. Craig *et al.*, *J. Biol. Chem.*, **168**, 393 (1947).

**Standardization.** Although the chemistry of penicillin has been fully worked out, no chemical method for its standardization has been found to be satisfactory and the potency is determined by microbiological assay. This is carried out by comparing the dose necessary to inhibit the growth of a sensitive strain of staphylococcus with the dose of a Standard Preparation of Penicillin necessary to produce the same degree of inhibition. The Standard Preparation is a sample of pure crystalline sodium salt of Penicillin-II or G, and the unit is defined under the Therapeutic Substances Act Regulations. The 1947 unit is the activity contained in 0.00065 mg. of the Standard Preparation. The unit is now the subject of international agreement, the U.S. Food and Drug Administration using a similar standard to the British.

For a description of the original method of assay, see *Lancet*, **2**, 177

(1941). An account of the various methods adopted by the laboratories concerned with the establishment of an international standard is given in *Quart. Bull. Hlth. Org. L.o.N.*, 12, 250 (1945-6).

In addition to the test for potency, penicillin must comply with tests for sterility, absence of undue toxicity, pyrogens, and moisture content. The test for pyrogens is carried out by injecting a solution intravenously into healthy rabbits and observing the body temperature. The average rise in temperature of three normal healthy rabbits, receiving a dose based on the bodyweight, should not be more than 0.6° C. The U.S. Food and Drug Administration prescribes a similar test and limits the increase in temperature to 1° C. The test for undue toxicity is carried out by injecting a specified amount intravenously into five healthy mice; all the mice must survive, but if only one of the five dies, the test can be repeated on a second group of mice; all five of the second group must survive.

*Clinical Uses.* Penicillin exerts both bacteriostatic and bactericidal actions against Gram-positive organisms, including *Staphylococcus*, *Streptococcus*, *Gonococcus*, *Bacillus anthracis*, *Pneumococcus*, *Actinomyces*, *Treponema pallidum* (the organism responsible for syphilis), and the causative organisms of gas-gangrene. For an account of its clinical uses, see *Penicillin, its Properties, Uses and Preparations* (The Pharmaceutical Press, London, 1946); and for report of British and American research, *The Chemistry of Penicillin*, edited by Hans T. Clarke, John R. Johnson, and Sir Robert Robinson (Princeton University Press).

On intramuscular injection, penicillin is rapidly absorbed into the blood-stream and rapidly eliminated from the body. This necessitates frequent intramuscular injections if a simple aqueous solution of the sodium salt is used. A preparation of the calcium salt suspended in arachis oil containing 4.5 per cent. of beeswax has been used to obtain more prolonged blood-levels and to reduce the number of injections necessary (see M. J. Romansky and G. E. Rittmann, *Science*, 100, 196 (1944)). A preparation consisting of a compound of procaine and penicillin in suspension in arachis oil has the advantages of easier administration and more prolonged therapeutic blood-levels.

(See Chain and Florey on penicillin in *Endeavour*, London, 3, 3 (1944); Coghill in *Chem. Eng. News*, 22, 588 (1944); Keefer and Anderson, *Penicillin in the Treatment of Infections* (Oxford University Press); Sir Alexander Fleming, *Penicillin—Its Practical Application* (Blakiston Co., Philadelphia); Antibiotics, and Gramicidin.)

**PENNYROYAL OIL** is distilled (0.1 to 0.2 per cent.) from the leaves and tops of the herb *Mentha pulegium*, a native of European countries. It is a pale yellowish, limpid, essential oil of mint-like odour, containing, in association with piperitone, 75 to 94 per cent. of a ketonic substance named pulegone; sp. gr. is 0.93 to 0.96 at 15° C., opt. rot. +13° to +35° at 20° C., b.p. 99° C. at 14 mm., and ref. ind. 1.475 to 1.486 at 20° C. It is produced in Spain, Southern France, and Africa, and is used in medicine and as an insectifuge. In one

determination, steam distillation of 100 kilograms of this oil yielded 350 to 500 grams of a dirty straw-coloured oil, having  $d$  0.8400 at 15.26° to 30° C. and acid value 0.1, containing 0.85 per cent. esters and 62 per cent. pulegone and piperitone. The oil is soluble in two parts of 70 per cent. alcohol.

**"PENTACETATE"** — A proprietary solvent composed of amyl alcohol with amyl acetate, for use in making cellulose lacquers.

**PENTACHLOROETHANE** — See Solvents.

**PENTACHLOROPHENOL** ( $C_6Cl_5OH$ ) — Used, in 5 per cent. solution in oil, as a wood preservative.

**"PENTALINE"** — See Solvents.

**PENTANE** — See Hydrocarbons.

**"PENTASOL"** — A proprietary solvent mixture of amyl alcohols made from the pentane of natural gas, for use in making cellulose lacquers; b.p. 116° to 136° C.

**PENTAVALENT (Penta)** — See Valencies.

**PENTENE ("Pental")** — See Amylene.

**"PENTHRINIT"** — German patented explosive for universal use, consisting of a mixture of 10 to 70 per cent. pentaerythritetranitrate ("Penthrit") and 90 to 30 per cent. respectively, nitroglycerine.

**PENTLANDITE** — A mineral double sulphide of iron and nickel, occurring in Norway and Argyllshire, containing 14 to 20 per cent. nickel.

**PENTOBARBITONE SODIUM (Pentobarbital Sodium, Soluble Pentobarbitone, "Nembutal")** ( $C_{11}H_{17}O_3N_2Na$ ) — A white, odourless, crystalline powder, being the monosodium derivative of 5-ethyl-5-(1-methyl-butyl)-barbituric acid; very soluble in water; soluble in alcohol; insoluble in ether. It is used in medicine as an hypnotic and for pre-operative sedation.

**PENTOSANS** — A group of hemicelluloses yielding pentose sugars on hydrolysis, and occurring in large amounts in cereal straws and brans. Strong sulphuric acid hydrolyses them to pentoses and then dehydrates the latter to furfural. This is the industrial method of preparing furfural. The most common pentosan is xylan, which yields xylose upon hydrolysis.

**PENTOSE** — Carbohydrates of the monosaccharide type containing five carbon atoms in the molecule, and possessing the general formula  $C_5H_{10}O_5$ . Carbon atoms 2, 3, and 4 are asymmetric and hence eight isomeric forms are possible, of which the best known are *l*-arabinose and *l*-xylose, which yield furfural when treated with strong hydrochloric acid. The pentosans extracted from plants are converted into pentoses by hydrolysis with dilute acid. Although not fermentable by yeast, the pentoses can be fermented by certain bacteria to yield a liquid fuel of an alcoholic nature. (See Carbohydrates.)

**PEPPER (Black Pepper)** — The dried, unripe fruits of *Piper nigrum*, a plant indigenous to South India and cultivated in the Malay Archipelago. It contains a colourless, crystalline alkaloid, piperine, and a yellowish volatile oil containing phellandrene, cadinene, and dipentene; sp. gr. 0.87 to 0.91 at 15°C.; opt. rot.  $-5^{\circ}$  to  $+12^{\circ}$ ; soluble in alcohol and ether. (See Piperine, and Piperidine.)

**PEPPERMINT OIL** — The volatile oil distilled from the leaves and flowering tops of *Mentha piperita* (Fam. Labiatae). It contains from 45 to 90 per cent. of menthol ( $C_{10}H_{20}O$ ), which separates on cooling the oil. There are several varieties of the oil. English and American oils contain from 40 to 69 per cent. of menthol together with some menthone, menthyl acetate, menthyl isovalerate, and limonene; sp. gr. 0.902 to 0.910 at 15°C.; opt. rot.  $-18^{\circ}$  to  $-32^{\circ}$ ; ref. ind. 1.460 to 1.470 at 20°C. Japanese and Chinese oils, obtained from *Mentha arvensis* var. *piperascens* and var. *glabrata*, contain about 85 per cent. of menthol. Brazilian peppermint oil contains about 50 per cent. of menthol. Dementholized oil is sometimes used as an adulterant. For a report on the characters of dementholized oil, see Benezet and Igolen, *Perf. and Essent. Oil Rec.*, **38**, 237 (1947). Wild Japanese oil has been stated to contain 20 per cent. of pulegone, 40 per cent. of *l*-menthone, 30 per cent. of *l*-limonene, and 5.8 per cent. of fatty acids.

Peppermint oil is used in medicine as a carminative and as a flavouring agent. It is also used in perfumery, for which purpose the American oil has been stated to be the most suitable. (See Spearmint Oil.)

**PEPSIN** — A nearly white amorphous substance, being the proteolytic enzyme contained in the gastric juice of animals. In the presence of acid (0.08 to 0.2 per cent. of hydrochloric acid) it converts proteins into soluble peptones. It is inactive in a neutral or alkaline medium. Pepsin of commerce is produced chiefly in the United States and is obtained from the gastric mucosa of sheep or calves. Pepsin is soluble in water and dilute acids; insoluble in alcohol; soluble in glycerin. Aqueous solutions are coagulated and inactivated by boiling. (See Enzymes, Gastric Juice, and Zymogens.)

**PEPTIZATION** — See Colloid Chemistry.

**PEPTONES** — Products of the hydrolysis of proteins; also result from the action of dilute acids or enzyme action of pepsin in the juices of the stomach upon the albuminous content of food. They are soluble in water, diffuse readily through vegetable parchment, are not precipitable by ammonium sulphate, and are not coagulated upon heating, so that they are in the best state for assimilation in the human economy.

**PER** — A prefix used in respect of compounds in which some element is above that of lower compounds of the same class or exhibits an unusually high valence; thus we have barium oxide ( $BaO$ ) and barium peroxide ( $BaO_2$ ), and, again, potassium chlorate ( $KClO_3$ ) and potassium perchlorate ( $KClO_4$ ).

**"PER-ABRODIL"** — See Diodone.

**"PERACTIVIN"** (**"Peraktivin"**) — A white powder consisting of a mixture of toluenesulphondichloramide and anhydrous sodium carbonate. Used for bleaching when it is dissolved in 10 per cent. sodium carbonate solution or 5 per cent. sodium hydroxide.

**"PER-ANDREN"** — See Testosterone.

**PERBORATE OF SODIUM** — See Sodium (Compounds).; and "Perox".

**PERBORIN** — Perborate of sodium.

**PERCARBONATES** — See Carbon Oxides.

**PERCHLORATES** — See Chlorine (Compounds).

**PERCHLOROETHANE** — See Hexachloroethane.

**PERCHLORETHYLENE** — See Tetrachloroethylene, and Solvents.

**"PERCLEN"** — See Tetrachloroethylene.

**PERCOLATION** — A process for the extraction of powdered vegetable drugs by moistening with the menstruum, packing the moistened material into a long column, and saturating with the solvent. After allowing the moistened drug to macerate for some time, the extraction process is continued by allowing the menstruum to drip slowly through the column. For a description of percolation in the manufacture of pharmaceutical preparations, see *Bentley's Textbook of Pharmacy*, revised by Davis (Baillière, Tindall and Cox, London).

**"PERCORTEN"** — See Deoxycortone Acetate.

**PERFUMES** — Preparations of a volatile nature consisting for the most part of pleasant, odoriferous substances dissolved in alcohol. Some of the better-known essences are obtained by distilling the flowers or flower-petals of plants with water, for example, attar of roses, while others are extracted therefrom by means of solvents such as light petroleum spirit or alcohol, the solvent being afterwards evaporated by distillation in a vacuum. Yet others, such as the tuberose and jonquil (the delicacy of which may be impaired by the distillation process or solvent action) are obtained by "enfleurage," a method which consists in pressing the flowers against a layer of cold fat (such as lard) or petroleum jelly spread over glass plates; or by drawing warm, moist air through the flowers and passing the current charged with the odoriferous principles over fatty layers, from which the perfume is subsequently extracted by strong alcohol. The subsequent evaporation of the alcohol yields the "quintessences" as residual products.

The odorous constituents of the apple include the amyl esters of formic, acetic, caproic, and caprylic acids, together with acetaldehyde and a small amount of geraniol. A synthetic mixture of apple oil is now made. Ethyl butyrate is the odoriferous constituent of the pineapple, and the pear owes its fragrance to amyl acetate. Coumarin, to which the Tonquin bean owes its fragrance, is now made artificially; so also vanillin, which gives its pleasant odour to the vanilla pod, is now largely made from eugenol (the chief constituent of oil of cloves).

Many butyrates occur frequently in nature, and are synthetically

prepared with a view to their use in preparing perfumes ; benzyl butyrate enters into the composition of artificial jasmin perfume ; geranyl butyrate, having an odour like that of the rose, is contained in good geranium oils ; phenyl butyrate is used as a base of artificial preparations of rose ; while rhodinol butyrate has a pleasant fragrance, and is employed in making " moss rose " compositions.

Geraniol, which is largely used in perfumery, can be prepared by polymerizing citronella oil, and subsequent fractional distillation. (See Geraniol, and Citronella Oil.) Hawthorn (" may blossom," aubépine) is reproduced by use of anisic aldehyde prepared by oxidation of aniseed oil. Modern lavender, as artificially prepared, consists of about 40 per cent. *l*-linalyl acetate, admixed with camphor, menthol, borneol, etc. (See Heliotropin, and Musk.)

An artificial essence of violets named ionone is made from citral (to which the odour of lemons and lemon grass is due), and there are many synthetically prepared perfumes, as distinct from those derived from flowers, or made in imitation of natural products, as, for example, heliotropin, sold as " white heliotrope." So again, a ketonic substance named irone is a fragrant oil made from the root of iris (orris), having the odour of the violet, which it acquires upon exposure to the hot rays of the sun, the freshly dug root having but a feeble perfume.

Among the synthetic perfumes may be mentioned " fragasol," which is the butyl ether of beta-naphthol, analogous to yara-yara and neroline, which are the methyl and ethyl ethers respectively. " Benzilisoegenol " has a fine carnation odour, and " rhodinol," or rose-aldehyde, is probably a mixture of aldehydes used in the manufacture of artificial attar of roses.

The aromatic aldehydes are largely used in the production and blending of perfumes, the more important ones being anisaldehyde, benzaldehyde, cuminaldehyde, salicylaldehyde, and phenylacetaldehyde (hyacinthin).

Stylosyl acetate has the perfume of the calyx of the rose, and amyl benzyloxide, which has a marked gardenia odour, is used for perfuming soaps, a trace of methyl-para-cresol improving it.

Methyl anthranilate (neroli oil) is a colourless, crystalline perfume made by heating anthranilic acid and methyl alcohol with sulphuric acid, followed by distillation ; while methyl benzoate (made similarly, using benzoic acid in place of anthranilic acid) is put up as " Essence Niobe."

In the perfume industry, phenylethyl alcohol of rose-like sweetness is produced by the reduction of the ester of phenylacetic acid by metallic sodium, the functional ester group being converted into the alcoholic radical.

Some of the essential oils constituting the bases of perfumes are obtained by pressure of the fruit rinds containing them, as, for example, the orange, lemon, and bergamot oils ; and many others such as eucalyptus oil, camphor oil, and the terpenes are commercially available in large quantities, and used either alone or in combination with other extractives in compounding various perfumes.

The use of isopropyl alcohol has been advocated as a solvent and

diluent in making perfumes, and its slight odour can be easily "touched up" by the use of certain esters.

Many chemical esters are used in perfumery, and, apart from the essential oils used in making perfumes and soaps, large quantities of these are used in compounding such drinks as lemonade and sundry alcoholic liqueurs, and for flavouring purposes, also in cooking, confectionery, and medicine, so that the trade in these oils, and the perfumes made from them, is one of large dimensions and importance.

*References:* Parry's *Cyclopædia of Perfumery* (J. and A. Churchill, London); W. A. Poucher's *Perfumes, Cosmetics, and Soaps* (Chapman and Hall, London); *Perfumery Synthetics and Isolates*, by Paul Z. Bedoukian (D. Van Nostrand Co., New York); Balsams, Benzyl Benzoate, Essential Oils, Ionone, Jasmine Oil, Odour Theory, Stearoptenes, and Terpeneol.

**"PERHYDROL"** — A name given to concentrated hydrogen peroxide (100 volume strength).

**PERI POSITION** — The 1, 8 positions in naphthalene (see same).

**PERICLASE** (MgO) — Crystal system No. 1, and sp. gr. 3.67. (See Magnesium.)

**PERIDOTE** (Mg<sub>2</sub>SiO<sub>4</sub>) — See Chrysotile, and Silicon.

**PERIDOTITES** — Name of igneous rocks of olivine character.

**PERILLA OIL** — A volatile oil distilled from the leaves of *Perilla nankinensis* (Japanese "Shiso"), containing perillaldehyde (C<sub>9</sub>H<sub>13</sub>.CHO), limonene, and some pinene. The dried leaves of *P. citriodora* yield 2 to 3 per cent. of volatile oil, containing 60 per cent. of citral and of sp. gr. 0.911 to 0.913.

The seeds of *P. ocimoides*, growing in North India, China, and Japan, contain from 38 to 49 per cent. of fixed oil; sp. gr. 0.932 to 0.945 at 15° C.; sap. v. about 189 to 197; i.v. (Wijs) 193 to 207; ref. ind. 1.4802 to 1.4818 at 25° C.; soluble in alcohol and ether.

Perilla oil is used in making printing inks and varnishes and, to some extent, as an edible oil in China and Japan.

**PERIODIC ACID** — See Iodine Compounds.

**PERIODIC LAW** — See Elements (Periodic Law).

**"PERMAC"** — A jointing material or cement, stated to be chemically neutral and not subject to oxidation, adhering firmly to glass, and used for making metal-to-metal joints capable of withstanding pressure.

**"PERMALLOY"** — A nickel-iron alloy of high magnetic permeability containing about 78.5 per cent. Ni.

**PERMANENT MOULD CASTING** — See Gravity-Die Casting.

**PERMANENT WHITE** — See Barium (Sulphate).

**PERMANGANATES** — See Manganese (Compounds).

**PERMEABILITY** — See Hydrogen, Occlusion, and Porosity.

**PERNAMBUCO** (Lima or Nicaragua Wood) — A red wood from *Cæsalpinia echinata*, which yields a red dye extract. There are various species of *Cæsalpinia*, all of which yield red dye woods. (See Brazil Wood Dyes.)

**PEROXIDE OF HYDROGEN** — See Hydrogen Peroxide.

**PEROXIDE OF SODIUM** — See Sodium (Compounds).

**PEROXIDES** — This term indicates oxides of higher degree than the ordinary oxides; for example, barium oxide ( $\text{BaO}$ ) is the ordinary barium oxide, whereas the peroxide (dioxide) is  $\text{BaO}_2$ . When treated with mineral acids (sometimes water, as with sodium peroxide) true peroxides yield hydrogen peroxide. Thus, lead dioxide and manganese dioxide are, therefore, not true peroxides.

There are some organic peroxides, among which may be mentioned acetyl peroxide,  $(\text{C}_2\text{H}_3\text{O})_2\text{O}_2$  (an explosive liquid body prepared from acetic anhydride by the action of barium dioxide); ethyl hydrogen peroxide,  $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{O}\cdot\text{H}$ ; diethyl peroxide,  $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{O}\cdot\text{C}_2\text{H}_5$ ; and acetone peroxide  $(\text{C}_3\text{H}_6\text{O}_2)_2$ . These liquids are more or less unstable, and are made by the agency of hydrogen peroxide in presence of potassium hydroxide. According to Mondain-Mouval and Quanquin, the oxidation of certain hydrocarbons (pentane, hexane, octane, petrol) by air at  $300^\circ\text{C}$ . or somewhat lower gives an oily liquid with marked oxidizing properties, which evolves hydrogen and gives sodium formate and methyl alcohol when treated with sodium hydroxide, and they conclude that this oily substance is a mixture of peroxides (*B.C.A.*, A, 1930, 1157). (See Ozonides, and Turpentine.)

**PERRY** — Fermented juice of pears.

**PERSIAN BARK** — See Cascara Sagrada.

**PERSIAN BERRIES** — See Frangula.

**PERSIAN RED** — Lead chromate.

**PERSIMMON** (*Diospyros kaki*) — A genus of Ebenaceæ, which furnishes a good timber, is a native of Japan and grows abundantly in Eastern Chekiang and in some parts of Western China. The Chinese prepare a lacquer from the fruit, the product being chiefly used as a water-proofing material for covering paper umbrellas and other articles. It is packed in "catties"—a catti =  $1\frac{1}{3}$  lbs. A sweetmeat known as "Figues-caques" is said to be made from the fruit in France.

**PERSOZ' REAGENT** — A mixture which at  $45^\circ\text{C}$ . will dissolve silk, but not wool; made by dissolving 10 grams of zinc chloride in 10 millilitres of water, and shaking up with 2 grams of zinc oxide.

**PERSULPHATES** — The persulphates of potassium, sodium, and ammonium, corresponding to persulphuric acid ( $\text{H}_2\text{S}_2\text{O}_8$ ), are crystalline compounds which can be prepared by electrolysis of their sulphates or bisulphates. They are valuable oxidizing and bleaching agents, and if kept dry and in the dark can be stored unaltered for long periods, but in ordinary aqueous solutions they decompose, and more rapidly as the temperature increases. This tendency to decomposition is restrained

to some extent by the addition of sodium sulphate. The sodium compound ( $\text{Na}_2\text{S}_2\text{O}_8$ ) is the most effective, and is used in one method of preparing hydrogen peroxide. (See Hydrogen Peroxide, and Sulphur Compounds.)

**PERU BALSAM** — See Balsams.

**PERUVIAN BARK** — See Cinchona.

**PERYLENE** — A hydrocarbon ( $\text{C}_{20}\text{H}_{12}$ ), m.p.  $264^\circ\text{C}$ ., yellowish in colour, can be prepared from beta-dinaphthol, which in turn is made by adding beta-naphthol to a hot dilute solution of ferric chloride. Numerous derivatives used as vat dyestuffs contain the perylene structure.

**PETALITE** ( $30\text{SiO}_2, 4\text{Al}_2\text{O}_3, \text{Na}_2\text{O}, 2\text{Li}_2\text{O}$ ) — A native silicate of aluminium and lithium of crystal system No. 5, and sp. gr. 2.5.

**PETHIDINE HYDROCHLORIDE** ( $\text{C}_{15}\text{H}_{21}\text{O}_2\text{N}, \text{HCl}$ ) — A colourless, crystalline powder, being the hydrochloride of ethyl 1-methyl-4-phenylpiperidine-4-carboxylate, prepared by reacting benzyl cyanide with  $\beta, \beta'$ -di( $\beta$ -chloroethyl) methylamine, hydrolysing the product, esterifying, and conversion to the hydrochloride; very soluble in water; soluble in alcohol; sparingly soluble in ether and acetone; soluble in chloroform; m.p.  $187^\circ$  to  $189^\circ\text{C}$ . Pethidine hydrochloride possesses analgesic and antispasmodic properties and is used in medicine in place of morphine to relieve pain. It is liable to produce addiction on prolonged administration but less so than morphine, see Himmelsbach, *J. Pharmacol.*, **79**, 5 (1943). For an account of its use for post-operative pain, see Batterman and Mulholland, *Arch. Surg.*, **46**, 404 (1943). It has been extensively used for the relief of labour-pains during childbirth, see Gallen and Prescott, *B.M.J.*, **1**, 176 (1944); Gilbert and Dixon, *Amer. J. Obstet. and Gynec.*, **45**, 350 (1943); and Spitzer, *B.M.J.*, **1**, 179 (1944). Owing to its potential use as a drug of addiction, pethidine hydrochloride has been added to the list of dangerous drugs subject to control by international agreement.

**PETITGRAIN OIL** — An essential oil distilled from a mixture of the leaves, young shoots, and unripe fruit of the bitter orange, *Citrus Aurantium* subsp. *amara* and sometimes from the sweet orange. It is a yellowish oil resembling neroli oil in colour; soluble in alcohol and ether; sp. gr. 0.867 to 0.895 at  $15^\circ\text{C}$ . Used in perfumery.

**PETROL** — See Motor Spirit.

**PETROLATUM** — A name given to yellow or white soft paraffin. (See Petroleum Jelly.)

**PETROLEUM (Rock or Mineral Oil)** occurs in the Miocene rocks of tropical and subtropical countries, and in smaller quantities in older rocks of colder countries. It is a natural, dark-coloured, oil-like deposit of hydrocarbon character, found mainly in rock formations of either the Tertiary or Carboniferous periods; sometimes occurring in beds or lakes as in Trinidad, and at other times flowing from clefts of rocks or

from deep wells, as in the northern parts of the United States, particularly between Pittsburg and Lake Erie. Deposits also occur in parts of Canada, Germany, Poland, Roumania, Galicia, Burma, Sarawak, Java, East Borneo, Assam, the Crimea, Trinidad, Barbados, Venezuela, Iran, Saudi Arabia.

The extent of petroleum occurrences in the United States can be comprehended by realizing that between 1859 and 1945 the following states each produced one million barrels or more of crude petroleum, namely, Texas (9·7), California (7·0), Oklakoma (5·5), Louisiana (1·7), Kansas (1·6), Illinois (1·2), and Pennsylvania (1·0).

PETROLEUM, WORLD PRODUCTION

Annual average for the three-year period 1937–1939  
Data arranged and rounded off by the Editor.

Country	Petroleum Millions of Barrels (One barrel equals 42 U.S.A. gallons or 306·6 pounds or 139·07 kilograms)			
Rumania .. .. .				49·0
U.S.S.R. .. .. .				203·6
U.S.A. .. .. .			1,252·3	
Mexico .. .. .			42·6	
Trinidad .. .. .			17·5	
			<hr/>	1,312·4
Venezuela .. .. .			193·5	
Colombia .. .. .			21·4	
Argentina .. .. .			17·3	
Peru .. .. .			15·6	
			<hr/>	247·8
Iran .. .. .			78·1	
Netherlands Indies .. .. .			58·4	
Iraq .. .. .			31·7	
			<hr/>	168·2
Sum of above .. .. .				1,981·0
WORLD PRODUCTION .. .. .				2,034·5

The figures for output of crude oil are given annually in the *C.T.J.*, and in *Minerals Yearbook* (U.S. Bureau of Mines).

The petroleum from all fields consists in the main of hydrocarbons, associated with small proportions of asphalt and compounds containing oxygen, nitrogen, and sulphur, and is worked on a large scale as the source of a number of valuable products. The crude oil can be purified to some extent by percolation through fuller's earth or specially prepared powdered bauxite, and there are various processes for desulphurizing petroleum, the "Frasch" process consisting of distilling the oil

over copper oxide, although for certain reasons this process is not suitable for the treatment of the crude Mexican oil. Sodium hypochlorite is another convenient purifying material for this purpose, and sodium plumbite is also used for the "sweetening" of petroleum, owing to its power of removing sulphur compounds such as hydrogen sulphide, and most mineral oils can be rendered colourless by the more or less prolonged action of sulphuric acid.

The hydrocarbons of many of the natural petroleum are of the same series, although contained in varying proportions; but while the American oils consist in the main of paraffin hydrocarbons, the Russian oil contains up to 80 per cent. of the general formula  $C_nH_{2n}$ , sometimes known as naphthenes, such as cyclopentane ( $C_5H_{10}$ ) and cyclohexane ( $C_6H_{12}$ ), which are isomeric with the olefines. That portion of Peruvian petroleum boiling between  $150^\circ$  and  $350^\circ$  C. is stated to contain some hydrocarbons having a pronounced odour of turpentine.

American Petroleum Institute Project No. 6 is on the subject of the hydrocarbons that can be isolated in petroleum. This Institute reports annually on the "proved oil reserves" and the 1949 estimate for the U.S.A. is 24,650,000,000 barrels. New discoveries in 1949 were twice as large as in any other year since 1938. More than 1.8 billion barrels were harvested in 1949 in U.S.A.

Crude petroleum is used to some extent as a substitute for coal in locomotives, has a sp. gr. ranging from 0.78 to 0.97 or more, and by fractional distillation yields a number of products, including the so-called petroleum ether, benzine, gasoline, kerosene, paraffin oil, heavy lubricating oils, petroleum jelly, paraffin wax, coke, and asphalt, which are described under their respective names. The various fractional distillates are further separated and refined by redistillation.

Crude petroleum is roughly classified as (1) paraffin base, (2) asphalt base, (3) mixed base, according to the predominating character of the oil.

The distillation of petroleum is frequently conducted by high vacuum methods, and although this is always accompanied by partial decomposition, it does not seriously affect the distillation so long as  $300^\circ$  to  $320^\circ$  C. temperature is not exceeded. Many types of plant have been designed to avoid cracking, working under an absolute pressure of about 2 mm. without steam or at about 20 mm. pressure with steam injection into the oil. High vacuum distillation is particularly valuable in respect of the heavy inferior asphaltic oils.

J. B. Hill discusses "The Petroleum Industry of 1935" (*Ind. Eng. Chem.*, **27**, 519 (1935)) under the topics, cracking, distillation, dewaxing, hydrogenation, solvent refining, liquefied gases, gasoline, and lubricating oil; and presents a map of the producing and refining areas of the United States. He lists the solvent extraction processes as those using (1) liquid sulphur dioxide, (2) sulphur dioxide-benzene, (3) phenol, (4) *beta*, *beta* *prime*-dichlorodiethyl ether ("Chlorex"), (5) nitrobenzene, (6) propane-cresylic acid, (7) furfural, and (8) liquid propane. The solvent refining of oils is described in *Ind. Eng. Chem.*, **27**, 836 (1935). (See Extraction).

*The Science of Petroleum* is a comprehensive treatise in 5 volumes of the principles and practice of production, refining, transport, and distribution, edited by A. E. Dunstan, B. T. Brooks, A. W. Nash, and H. T. Tizard (Oxford University Press), and further references are *The Chemical Technology of Petroleum*, by W. A. Gruse and D. R. Stevens (McGraw-Hill Book Co., New York); *The Chemical Constituents of Petroleum*, by A. N. Sachanen (Reinhold Publishing Corp., New York); and *Chemical Refining of Petroleum*, by V. A. Kalichevsky and B. A. Stagner (Reinhold Publishing Corp., New York).

The flash-points fixed for fuel by the British authorities are as follows: Lloyd's Register of Shipping, 150° F.; London County Council, 150° F.; and the Admiralty, 175° C. (See Flash-Point.)

The spontaneous ignition temperatures of various fuel oils in an atmosphere of oxygen have been determined as follows: Petrol, 270° and 279° C.; kerosene, 251° to 253° C.; gas oil, 254° C.; residual oils, 259.5° to 269° C.; commercial benzol, 566° C.; commercial toluol, 516° C.; gasworks tar creosote, 415° to 473° C.; creosote from low-temperature tars, 290° to 350° C.; shale oil, 251° C.; whale oil, 273° C.

The International Union of Pure and Applied Chemistry, July, 1928, adopted a classification for petroleum products as follows: Spirits (essences), upper limit of distillation 225° C.; lamp oils, lower limit for ignition 25° C.; and combustible residue, lower limit for ignition 50° C.

The low-boiling distillate produced from many crude petroleum requires no chemical treatment, and is largely used as motor spirit; but the "white spirit" and "kerosene" which follow (and are used in lamps) are refined by filtration through powdered bauxite or fuller's earth, which removes the sulphur compounds and can be regenerated for renewed use by heating.

**Paraffin wax** is separated from the higher distillate portion containing it, by cooling to 7° C., and squeezing out the heavy associated oil, which is utilized as lubricating oil after redistillation. Both paraffin and kerosene can be obtained white by filtration through bauxite.

**Petroleum coke (Pitch)** is finally left in the retort, and, the former being very pure, finds a ready sale to the manufacturers of electric-light carbons and carbon crucibles, whilst the pitch can be used either as fuel or can be oxidized or sulphurized, and thus utilized in making artificial asphalt.

**Cracking of Petroleum** — Serious decomposition of petroleum does not occur below 300° to 320° C., but when "cracked" at about 700° to 750° C., most of them yield a distillate containing toluene and benzene but low in naphthalene.

By the cracking of the high-boiling distillates from crude petroleum, namely, those boiling at 225° C. and upwards, low-boiling fractions belonging mostly to the aliphatic or paraffin series of suitable character for use in internal combustion engines are obtained. This is carried out by subjecting them to a high temperature and pressure in a pipe-still, and then passing into a reactor, where the "cracking" takes place,

the light oils being separated from the heavy residues in a rectifying column, a residue of coke being left in the "reactor." Cracking of petroleum can also be carried out in the vapour phase, and in some processes various agents are used as catalysts. It is estimated that as much as 1,750,000 barrels per day of petroleum fractions can be processed by catalytic processes alone.

The catalysts are natural clays, synthetic aluminium oxide-silicon oxide or magnesium oxide-silicon oxide combinations, or bauxite (see R. W. Porter in *Chem. and Met. Engr.*, **53**, No. 4, 94 (1946)). The Houdry process, introduced in 1938, is of the fixed-bed type, where granules or beads of the catalyst are placed in a shell through which the oil vapour or air flows in sequence. The shell is surrounded by a liquid medium to *absorb* heat during the cycle of regeneration (burning of the deposit of carbon) of the catalyst, and to *supply* heat to the oil vapour during the cycle of cracking and to the air required for burning the carbon during the regeneration cycle.

The Thermoform process (1942) uses a continuously moving, downward stream of catalyst, which is withdrawn from the bottom of the reaction compartment and transported to the top by exterior bucket elevators. The flow of charge and catalyst may be either counter-current or concurrent. The catalyst is regenerated in principle as in the Houdry process.

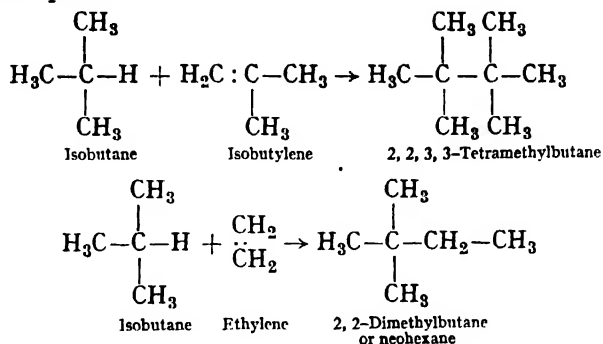
The fluid catalytic process (1942) commonly employs a continuously upward moving, dense, thick, turbulent stream of finely divided catalyst where the cracking occurs, and above this bed one of dilute, thin stream of suspended catalyst which is removed by cyclones and recirculated. From the former or main bed the spent catalyst is continuously withdrawn and stripped of its hydrocarbon content by steam. Then to this catalyst hot air is fed to burn the carbon and regenerate the catalyst, after which the catalyst is run while still hot into the oil feed, and thence—both catalyst and oil—to the reaction compartment. The transfer of the heat of combustion of the carbon deposit supplies directly the heat necessary for preheating, vaporizing, and cracking the oil.

The "cracking" for conversion of the higher fractions of petroleum into motor spirit produces large quantities of permanent gas containing from 10 to 60 per cent. of olefine gases, including ethylene, propylene, and the butylenes, constituting an important crude material for the manufacture of secondary and tertiary alcohols, etc. (See "Development of the Oil Cracking Art," by P. C. Keith and W. B. Montgomery (*Ind. Eng. Chem.*, **26**, 190 (1934)); "Pyrolysis of Hydrocarbons" (*Ind. Eng. Chem.*, **40**, 1660 (1948)); *Chemistry and Technology of Cracking*, by A. N. Sachanen and M. D. Tilicheyev (Reinhold Publishing Corp., New York).

Special fuels for aviation are required to have a high octane rating (see same). These are made by various reactions involving hydrocarbons, such as (a) alkylation, and (b) polymerization.

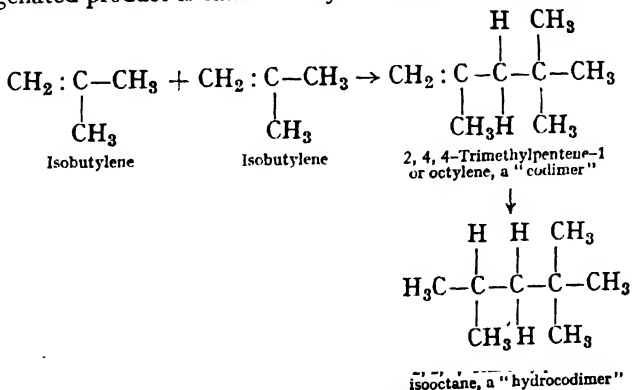
In *alkylation*, a paraffin hydrocarbon (in excess) and an olefin are combined—the product being called "alkylate." The process uses a

catalyst, either anhydrous hydrofluoric acid or concentrated sulphuric acid. Examples :



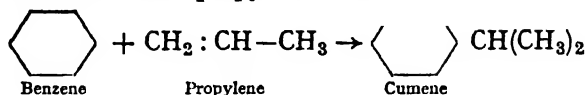
The temperature required is approximately 950° F. and the pressure 3,000 to 5,000 lb./sq. in. For the production of the required isobutane from normal butane an isomerization reaction is utilized, the catalyst being a liquid combination of aluminium chloride and hydrogen chloride, both anhydrous ; the temperature 125 to 150° F. ; and the pressure 150 to 500 lb./sq. in. For isobutylene from normal butane, the dehydrogenation reaction uses as catalyst chromic oxide supported on aluminium oxide, in the form of pellets ; a temperature of 950 to 1200° F. ; and a pressure of 25 to 50 lb./sq. in. Hydrogen gas is a by-product.

*Polymerization* of two moles of C<sub>4</sub>-olefin hydrocarbon proceeds with concentrated sulphuric acid or solid phosphoric acid at 300 to 350° F. and 300 to 350 lb./sq. in. to yield a monoolefin hydrocarbon ("codimer") that must be hydrogenated for use in a finished fuel. The hydrogenated product is called a "hydrocodimer." Example :



The hydrogenation reaction (last one above) is conducted by reacting the codimer with hydrogen gas in the presence of reduced nickel catalyst on a supporting carrier, at 400° F. and 60 lb./sq. in. pressure.

Cumene is made by a process similar to that for alkylation by the reaction of benzene and propylene, thus :



The octane ratings (O.R.) of some of these special hydrocarbons are as follows :

2,2,4-Trimethylpentane (isoöctane)	..	100	O.R.
2,2,3-Trimethylpentane	..	99.9	O.R.
2,3,3-Trimethylpentane	..	99.4	O.R.
2,3,4-Trimethylpentane	..	95.9	O.R.
2,2,3,3-Tetramethylbutane	..	93	O.R.
2,2-Dimethylpentane	..	93	O.R.
2,2,3-Trimethylbutane (triptane)	..	101	O.R.
2,2-Dimethylbutane (neohexane)	..	95	O.R.
Benzene	..	100	O.R.

**“ Polymerized ” Gasoline** — See Hydroforming, Platforming, and Polymerization (Catalytic).

**Catalytic Oxidation of Petroleum** — Fatty acids can, it is stated, be obtained from petroleum hydrocarbons by catalytic oxidation, using air or oxygen in association with certain lead or mercury compounds (which apparently dissolve in the products of the process) at a temperature of 115° to 120° C., and under a pressure of three atmospheres, with agitation in the presence of water for some seven hours. The oxidation products have been stated at from 7 to 20 per cent. water, 25 to 40 per cent. lower fatty acids, with small amounts of aliphatic aldehydes and ketones, from 50 to 78 per cent. of higher fatty acids, and 10 to 15 per cent. of unsaponifiable matters. The products are fractionated by distillation, and the higher fatty acids obtained mixed with 10 to 20 per cent. of tallow or coconut oil fatty acids can be used to make soap.

By another process, that of passing the vapour of petroleum hydrocarbons and air through a series of catalytic agents (uranium and molybdenum oxides) at from 240° C. to something under 500° C., oxidation of the aliphatic hydrocarbons occurs, and among the products are certain oxygenated acids of aldehydic character, which admit of saponification with calcium hydroxide and caustic soda. These acids are of a resin-like character, and the soaps, as also certain other associated products formed from them, have commercial value as lubricants, and frothing oil for use in the field of oil flotation. (See Oxo Reaction.)

Fatty acids can also be obtained by the chlorination of certain paraffin hydrocarbons at 160° C., subsequent elimination of the hydrogen chloride thus produced, and oxidation of the resulting olefine by means of potassium permanganate or ozone.

**Origin of Petroleum** — One supposition is that mineral oil and natural gas are formed in nature by the action of water on metallic carbides present in the heated interior of the earth ; another that it is the product of volcanic action ; but the balance of opinion is in favour of the view

that they are derived from organic matters by chemical changes operating over long periods of time. As all petroleum contains so-called algæ wax, one hypothesis favours enormous masses of algæ accumulated over immense periods of time in marshy areas as its originating material. There is also a "resin" theory, and the further view that petroleum, like all the carbon deposits having a vegetable origin, is derived from cellulose, the composition of which shows that it can supply sufficient carbon and hydrogen to account for the quantities of these elements found in the liquid and gaseous hydrocarbons, although the changes which the cellulose in that case must have undergone are different from those which produce coal, lignite, or peat. The close similarity between the oils from the Balkash Sapropelite and the natural petroleum fractions has been viewed as giving experimental support to the organic origin hypothesis.

Artificial petroleum is produced by hydrogenating acetylene at high temperatures and pressures, and this has led to the suggestion that the natural petroleum has been formed by some such process.

Fischer (of Germany), in respect of his process for the synthesis of liquid fuel, has stated that it renders possible the production of any aliphatic petroleum product in the pure state, and that it is based in the main upon reduction of a mixture of carbon monoxide and hydrogen in presence of a catalyst (iron or cobalt) at a temperature below 300° C. (See Fuel (Liquid), and "Synthol.")

"Dry" natural gas from petroleum wells rarely contains more than 0.5 gallons of gasoline per 1,000 cubic feet, and "casing-head" gas up to 10 to 15 gallons. Natural gas invariably accompanies petroleum in oil-sands, and is extracted by compression and absorption methods. The casing-head gas consists of a mixture of the lower members of the paraffin series, including methane, ethane, propane, butane, pentane, etc., and can be used in some cases for heating purposes by combustion. The absorption method consists in scrubbing the gas with a suitable solvent oil and subsequently distilling.

*References:* "Recent and Future Developments in Petroleum Refining," by Simard (*Chem. and Ind.*, **56**, 520 (1937)) contains octane ratings of hydrocarbons; *A Treatise on Petroleum*, by Boverton Redwood (C. Griffin and Son, London); *Handbook of the Petroleum Industry*, by D. T. Day (John Wiley and Sons, New York); *The Examination of Petroleum*, by Hamar and Padgett (McGraw-Hill Book Co., New York); *Low-Temperature Distillation*, by North and Garbe (Sir Isaac Pitman and Sons, London); *The Chemistry of Petroleum and its Substitutes*, by C. K. Tinkler (Crosby Lockwood and Co., London); *The Petroleum and Allied Industries*, by J. Kewley (Baillière, Tindall and Cox, London); *Petroleum Technology*, by L. Gurwitch and H. Moore (Chapman and Hall, London); *Petroleum and Its Products*, by W. A. Gruse (McGraw-Hill Book Co., New York); *A.S.T.M. Standards on Petroleum Products and Lubricants* (American Society for Testing Materials, Philadelphia); *UOP Laboratory Test Methods for Petroleum and Its Products* (Universal Oil Products Co., Chicago). (See also Asphaltenes, Benzene, Shale, and Torbanite.)

**PETROLEUM ETHER** (Canadol, Ligroin) — The fractional distillate from petroleum, b.p. 40° to 70° C., and sp. gr. 0.635 to 0.660, purified by washing with sulphuric acid, then with soda, and subsequent redistillation. Various fractions, designated by their boiling ranges or trade names, are available, *e.g.*, petroleum ether 40–50. It contains a large proportion of the lower paraffin hydrocarbons (hexane, heptane, etc.), is very inflammable, and constitutes a widely-used volatile solvent.

**PETROLEUM JELLY** (Petrolatum) is an emulsion of soft paraffins (highly saturated hydrocarbons) dispersed in heavy oils, the viscosity of which increases gradually with decreasing temperature until the “gel” state is reached. There is no separation of crystalline wax, which is only obtained upon distillation of the jelly (in the distillate). It is a high-boiling distillation product made from the still residue left after the distillation of petroleum, decolourized by filtration in a heated state through fuller’s earth or animal charcoal, and used as a lubricant, rust preventive, in making ointments, leather dressing, polishes, and as a perfume extractor in enfleurage. (See “Vaseline.”)

**PEWTER** — See Alloys and Tin.

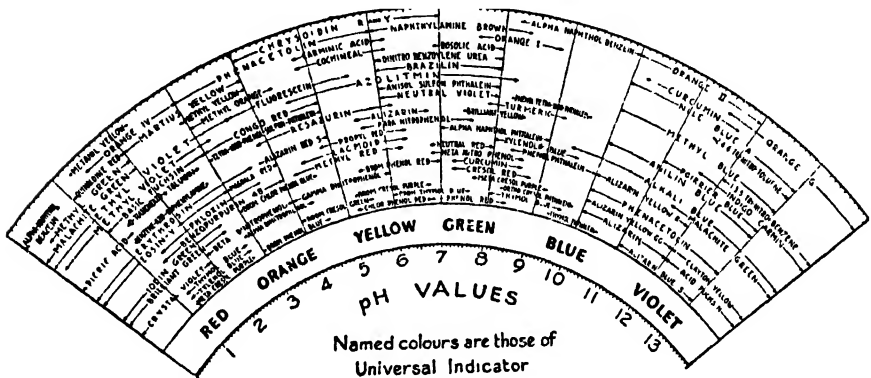
**pH VALUE** — A term used to express the acidity or alkalinity of solutions, being the reciprocal of the logarithm of the hydrogen-ion concentration  $[H^+]$  in gram-ionic weights per litre, thus :

$$pH = \log \frac{1}{[H^+]}$$

When the concentration of hydrogen-ions in a water solution equals the concentration of hydroxyl-ions in the same solution, we know that each concentration is  $10^{-7}$  gram-ions. In this example  $10^{-7}$  is the hydrogen-ion concentration, and 7 is the pH. For solutions on the acidic side of neutrality pH is *less* than 7, and for those on the basic side pH is *more* than 7. For one-hundredth normal hydrochloric acid pH=2 and for one-tenth normal acetic acid pH=3, and for one-hundredth normal sodium hydroxide pH=12 and for one-tenth normal ammonium hydroxide pH=11. If the hydrogen-ion concentration of the blood rises so that the normal pH of 7.4 is changed to even 6.95, coma and death result. If, on the other hand, the hydrogen-ion concentration falls so that the pH is changed to even 7.7, tetanic convulsions follow. This is in regard to the blood, but other body fluids have different requirements for the maintainance of health, for example, gastric juice pH 1.7, pancreatic juice 7.8, intestinal juice 7.7, urine 5.0–7.0, and milk 6.5–7.0. Animal tissues and fluids have prevailing values of pH about in the range 7.0 to 7.5. But the corresponding value for plant tissues and fluids is 5.2. It has been demonstrated that for each plant there is a pH value or narrow range which produces the best growth. Thus, clover, alfalfa, and timothy grow best when the pH of the soil is 6.0–8.0. For the cereals, potatoes,

and cotton the range is about the same. But orange and lemon grow best in soils where the pH is 5.0-7.0, rhododendron 5.0-6.0, and holly 4.0-6.0. Other examples of the importance of pH are baking of foods, purification of water, fermentations of sugar and starches, bleaching, dyeing, and the production of numerous chemicals. (See *Colorimetric and Potentiometric Determination of pH*, by I. M. Kolthoff (Chapman and Hall, London); *Determination of Hydrogen Ions*, by W. M. Clark (Williams and Wilkins Co., Baltimore); *pH and Its Practical Application*, by F. L. LaMotte, W. R. Kenny, and A. B. Reed (Williams and Wilkins Co., Baltimore); *Hydrogen-Ion, Indicators, and Volumetric Analyses*.)

### CHART OF INDICATORS



Courtesy of Hartman-Leddard Company, Incorporated, Philadelphia.  
An enlargement is printed in full spectrum colours.

### SOME pH APPLICATIONS

INDICATOR	CLOUR	pH	pH	WATER SOLUTION
	YELLOW	0	ACIDIC	
METHYL VIOLET	GREEN			1 HYDROCHLORIC ACID, ONE-TENTH NORMAL
	BLUE-VIOLET	2		2 CITRIC ACID, ONE-TENTH NORMAL
				3 ACETIC ACID, ONE-TENTH NORMAL
METHYL ORANGE	RED	3		ALSO, ALUMINIUM CHLORIDE, ONE-TENTH NORMAL
	YELLOW			
	COLOURLESS	5		5 BORIC ACID, ONE-TENTH NORMAL
PARA-NITROPHENOL	YELLOW	7	NEUTRAL	7 WATER, PURE
PHENOLPHTHALEIN	COLOURLESS			9 SODIUM BORATE, ONE-TENTH NORMAL
	RED	10		
ALIZARIN YELLOW	YELLOW			11 AMMONIUM HYDROXIDE, ONE-TENTH NORMAL
	BLUE	12		12 TRISODIUM PHOSPHATE, ONE-TENTH NORMAL
INDIGO-CARMINE	BLUE			13 SODIUM HYDROXIDE, ONE-TENTH NORMAL
	VIOLET	14	BASIC	

**Ph** — A symbol used for phenyl ( $C_6H_5$ ) radical.

**PHAGOCYTES** — Amœboid cells, also called leucocytes (the white corpuscles of the blood), capable of ingesting or destroying bacteria and viruses in the blood ; this phagocytic activity is said to be increased by other substances known as Opsonins. (See Bacteria.)

**PHARMACY** — The preparation of medicinal agents. The word pharmacy is derived from the Greek *pharmakon*, a drug, and the practice of pharmacy depends upon a study of the various substances used in the treatment of disease. Pharmaceutical chemistry comprises a study of the inorganic and organic compounds used in medicine ; the study of the cultivation and preparation of crude drugs of animal and vegetable origin is known as Pharmacognosy. The formulation of these substances into suitable medicinal agents is known as Pharmaceuticals, which also includes the preparation of sterile medicaments for parenteral use and micro-biological preparations such as vaccines and sera. In addition, the practice of pharmacy requires a knowledge of the normal functioning of the body (Physiology) and the mode of action of drugs (Pharmacology).

In Great Britain and the British Empire the *British Pharmacopœia*, published under the direction of the General Medical Council, provides the official standards for substances in common use in medicine and pharmacy. The information of the *British Pharmacopœia* is supplemented by the *British Pharmaceutical Codex*, published by the Pharmaceutical Society of Great Britain. In the United States the corresponding authorities are the *United States Pharmacopœia* and the *National Formulary*. The *Extra Pharmacopœia* (Vol. I), originally written by W. H. Martindale and now published by the Pharmaceutical Society of Great Britain, provides a summary of the information contained in the British and foreign pharmacopœias together with abstracts from medical and pharmaceutical literature. See also the *United States Dispensatory* (Lippincott and Co., Philadelphia and London) ; *Remington's Practice of Pharmacy* (Lippincott and Co., London) ; *Bentley's Textbook of Pharmacy* revised by H. Davis (Baillière, Tindall and Cox, London) ; *New and Non-Official Remedies* (Amer. Med. Ass.) ; *Bioassays: A Handbook of Quantitative Pharmacology*, by J. C. Munch (Baillière, Tindall and Cox, London) ; and *Pharmaceutical Formulas* (Chemist and Druggist, London).

**PHASE RULE** — This is a general law of systems in equilibrium which defines the conditions of the equilibrium as a relationship between the number of phases and the number of components of the system. In any system at equilibrium the number of *degrees of freedom* (F) plus the *number of phases* (P) is equal to the *number of components* (C) plus a *number* (n). Stated concisely :  $F + P = C + n$ .

In this generalization, stated by J. Willard Gibbs in 1876, the number of degrees of freedom refers to the independently variable conditions such as temperature, pressure, concentration, gravity, magnetic fields, electrical fields, etc., which must be arbitrarily fixed in order that the system may be perfectly defined ; the number of phases refers to

the number of individual regions which within themselves are physically and chemically homogeneous. Since all gases are miscible there can be only one gaseous phase but there may be several co-existing liquid and solid phases. The number of components refers to the minimum (smallest) number of chemical constituents which must be specified in order to describe the composition of each phase that is present, and applies only to those constituents whose concentration can undergo independent variation in the different phases. The number ( $n$ ) refers to the number of variable conditions, *in addition to composition*, which influence the equilibrium.

To illustrate the use of the phase rule and the meaning of the terms consider water (see Water for diagram) in equilibrium at temperatures below its decomposition temperature and at normal pressures. The number of constituents taking part in the equilibrium between the various phases is only one, namely, the chemical substance, water. Hydrogen and oxygen, the constituent elements of water, are not regarded as components because they are not present as *free* elements in the system. Furthermore, hydrogen and oxygen are combined in a definite proportion to form water and their amounts in water cannot be varied independently. If the system is restricted to a given locality the independently variable conditions are only temperature and pressure, since the other variables are then constant. The water system under the conditions imposed can exist in three phases, gas, liquid, or solid, and the phase rule will be  $F+P=1+2$ . When two phases are present (liquid-vapour, solid-vapour, or solid-liquid)  $F+2=1+2$  and  $F=1$ . This means that the system is completely defined when any two phases are specified *and* either the pressure or temperature. An examination of the water diagram shows that any point on the curves becomes fixed by stating either the temperature or the pressure. If all three phases are present (ice-water-vapour) then  $F+3=1+2$  and  $F=0$ . This is the triple point where the temperature and pressure are both fixed.

To further illustrate these principles consider the decomposition of magnesium carbonate into magnesium oxide and carbon dioxide according to the following equation :  $\text{MgCO}_3 (\text{solid}) = \text{MgO} (\text{solid}) + \text{CO}_2 (\text{gas})$ . At each temperature there is an equilibrium where all three substances are present. Although all three substances take part in the equilibrium, they are not all to be regarded as components since they are not all mutually independent of each other. The above equation, showing the relation that exists between the various constituents and phases, indicates that if any two constituents are taken, the composition of the third is fixed or defined. The smallest number of independently variable constituents by means of which the composition of each phase can be expressed is two in this equilibrium. The actual choice of the two components is not important as the third component is always given by the above chemical equation. In this system the phase rule is  $F+P=2+2$  and the following relations exist : when  $P=1$  then  $F=3$  ; when  $P=2$  then  $F=2$  ; when  $P=3$  then  $F=1$  ; when  $P=4$  then  $F=0$ .

the cresols, are less poisonous than phenol, and are used in making disinfectants, sheep dips, insecticides, larvicides, weed-killers, and cutting compounds for engineering purposes, as they form good emulsions in aqueous soap solutions. (See Phenols, and Xylenols.)

**PHENOLPHTHALEÏN** ( $C_{20}H_{14}O_4$ ) — A white or slightly off-white, crystalline or amorphous powder, prepared by heating phenol with phthalic anhydride in the presence of sulphuric acid; almost insoluble in water; soluble in alcohol and ether; m.p. about  $260^{\circ}C$ . It is used in medicine as a purgative and in analytical chemistry as an indicator. A 0.5 per cent. solution in 50 per cent. alcohol gives a strong pink colour when rendered alkaline. (See Phthaleïns, Indicators, and Volumetric Analysis.)

**PHENOL RESINS** — See Gums and Resins.

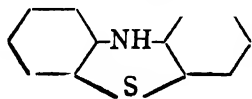
**PHENOLS** — A series of bodies, some being liquids and some solids, possessing antiseptic properties. They are termed monohydroxy when they contain one hydroxyl group (directly connected to nuclear carbon atoms); dihydroxy when two are present; trihydroxy when three groups are present; and polyhydroxy when they contain many such groups. Catechol ( $C_6H_4(OH)_2$  (1, 2)) is a dihydroxy phenol; pyrogallol ( $C_6H_3(OH)_3$  (1, 2, 3)) is represented as a trihydroxy member; and quercitol ( $C_6H_7(OH)_5$ ) as a polyhydroxy phenol.

Ordinary phenol or carbolic acid ( $C_6H_5OH$ ) is the active principle of crude carbolic acid as obtained from coal-tar fractional distillation. During World War I large quantities of phenol were prepared synthetically from benzene, proceeding through benzenesulphonic acid. Other processes for the synthesis of phenol are based respectively on the hydrolysis of monochlorobenzene by means of steam, and upon the direct oxidation of benzene in the vapour phase, using air in presence of a catalyst. The synthetic processes form part of the subject of No. 6, Technical Records of Explosives Supply, 1915–1918 (H.M. Stationery Office). (See Neuworth (*J. Amer. Chem. Soc.*, **69**, 1653 (1947)).)

In the pure state phenol is a white, poisonous, deliquescent, colourless, crystalline substance, of sp. gr. 1.07, b.p.  $181.4^{\circ}C$ ., m.p.  $42^{\circ}C$ .; is soluble in water (1 : 15) at  $16^{\circ}C$ ., and the crystals are liquefied by a little water. It is also readily soluble in alcohol and ether, possesses strong antiseptic properties, but is corrosive to the skin and very poisonous. It is used in the manufacture of disinfectant preparations, dyes, picric acid, salicylic acid, and other compounds, also in compounding synthetic resins.

Phenols of the naphthalene series are described as naphthols, and those from toluene as cresols. Phenolic bodies include cresol ( $C_7H_8O$ ), xylol ( $C_8H_{10}O$ ), catechol ( $C_6H_6O_2$ ), cumenol ( $C_9H_{12}O$ ), carvacrol ( $C_{10}H_{14}O$ ), guaiacol ( $C_7H_8O_2$ ), and thymol ( $C_{10}H_{14}O$ ). (See Carbolic Acid, Tars, and Tricresyl Phosphate.)

**PHENOTHIAZINE**



— Yellow leaflets, crystal-

lizable from alcohol, of melting point  $180^{\circ}\text{C}.$ , and subliming at  $371^{\circ}\text{C}.$  Used to combat internal parasites that attack cattle and sheep.

**PHENOXIDES** — See Phenolates.

**PHENOXYETHANOL** ("Phenoxetol") ( $\text{C}_6\text{H}_5\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{OH}$ ) — A colourless mobile liquid, namely  $\beta$ -phenoxyethyl alcohol, having a slight and pleasant odour; slightly soluble in water. Used in medicine as an antiseptic against *Pseudomonas pyocanea* and other gram-negative organisms (see H. Berry, J. Gough, and B. M. Still, *Lancet*, **2**, 175(1944)).

**PHENYL** — The univalent radical  $-\text{C}_6\text{H}_5$ , as contained, for example, in phenol ( $\text{C}_6\text{H}_5\text{OH}$ ), and in aniline ( $\text{C}_6\text{H}_5\text{NH}_2$ ) (phenylamine).

**PHENYL SALICYLATE** (Salol) ( $\text{C}_6\text{H}_4(\text{OH})\cdot\text{COOC}_6\text{H}_5$  (1) (2)) — A white, crystalline substance, prepared by treating a mixture of sodium salicylate and sodium phenoxide with phosphoryl chloride; insoluble in water; soluble in alcohol, ether, and chloroform; m.p.  $42^{\circ}$  to  $43.5^{\circ}\text{C}.$ ; b.p. about  $173^{\circ}\text{C}.$  It was formerly used in medicine but has been shown to pass through the body completely unchanged. It is sometimes used for coating tablets which are required to pass unchanged through the stomach but disintegrate in the small intestine.

**PHENYLACETALDEHYDE** (Alpha-Toluyaldehyde) ( $\text{C}_6\text{H}_5\text{CH}_2\text{CHO}$ ) — A colourless liquid of sp. gr. 1.03 and b.p. about  $193^{\circ}\text{C}.$ ; used in perfumery, having an odour like that of hyacinth; soluble in alcohol and ether.

**PHENYLACETIC ACID** (Alpha-Toluic Acid) ( $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ ) — A white crystalline substance, soluble in alcohol and ether, used in perfumery; m.p.  $76^{\circ}\text{C}.$

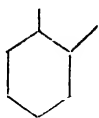
**PHENYLHYDRAZINE** ( $\text{C}_6\text{H}_5\text{NHNH}_2$ ) — A colourless crystalline body melting at  $19.6^{\circ}\text{C}.$  and reducible to aniline and ammonia. Phenylhydrazine is an important reagent for testing (1) for the carbonyl group ( $>\text{CO}$ ) of aldehydes and ketones, phenylhydrazones being formed generally of characteristic melting-points; and (2) for sugars, osazones (see same) being frequently formed. (See Hydrazones.)

Phenylhydrazone of			Melting-Point, $^{\circ}\text{C}$
Acetaldehyde .. ..	..	..	99
Acetone .. .. .	..	..	27
Acetophenone .. ..	..	..	105
Benzaldehyde .. ..	..	..	155
Benzophenone .. ..	..	..	137

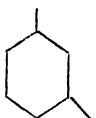
**PHENYLHYDRAZONES** — See Phenylhydrazine.

**PHENYLAMINE** (Aniline) ( $\text{C}_6\text{H}_5\text{NH}_2$ ) — See Aniline.

**PHENYLENE** — The divalent radicals  $C_6H_4$ , of which there are three, namely,



ortho-



meta-



para-

**PHENYLENEDIAMINES** ( $C_6H_4(NH_2)_2$ ) — There are three isomers (*o*, *m*, and *p*), all colourless, crystalline, unstable substances, soluble in alcohol, ether, and water. The *ortho* compound is used in preparing colours for skins; the *meta* in making azo-dyes; and the *para* in the synthesis of various dyes and for colouring skins and hair.

**PHENYLETHYL ALCOHOL, ALPHA (Methylphenyl Carbinol)** ( $C_6H_5.CH(OH).CH_3$ ) — A secondary alcohol (analogous to the alcohols of the fatty series) which can be prepared synthetically, and is used in perfumery. It occurs to the extent of some 75 per cent. in rose oil, and is obtained by the maceration extraction process, but not in that resulting from direct steam distillation.

**PHENYLMERCURIC NITRATE** ("Merfenil") ( $C_6H_5.HgOH.C_6H_5.HgNO_3$ ) — A white, odourless, crystalline powder, being a basic phenylmercuric nitrate obtained by reacting nitrogen tetroxide and diphenylmercury in ice-cold chloroform solution, and recrystallization from alcohol; slightly soluble in water; sparingly soluble in alcohol; soluble in glycerin and fixed oils; m.p.  $185^\circ$  to  $190^\circ C.$ , with decomposition. Phenylmercuric nitrate possesses bacteriostatic and fungicidal properties and is used in medicine as an antiseptic. For an account of its uses in medicine, see E. A. J. Byrne, *Brit. Med. J.*, **1**, 90 (1947). Phenylmercuric acetate and phenylmercuric chloride are also used for similar purposes, the latter having been suggested for the impregnation of handkerchiefs as a prophylactic measure against the common cold.

**PHENYTOIN SODIUM** (Soluble Phenytoin, Diphenylhydantoin Sodium, "Epanutin") ( $C_{15}H_{11}O_2N_2Na$ ) — A white, odourless powder, being the monosodium derivative of 5,5-diphenylhydantoin; very soluble in water; soluble in alcohol; insoluble in ether and chloroform. It has an hypnotic action and is used in medicine as a sedative for the treatment of epilepsy.

**PHLOGOPITE** ( $3(K_2,H_2)O.6(Mg,Fe)O.(Al_2,Fe_2)O_3.6SiO_2$ ) — A micaceous mineral of crystal system No. 5, and sp. gr. 2.8 to 3.2, constituting the main Canadian supply. (See Mica.)

**PHLORIDZIN** ( $C_{21}H_{24}O_{10}.2H_2O$ ) — A poisonous, crystalline glucoside that melts at  $108^\circ$ , then solidifies at  $130^\circ$ , and remelts at  $170^\circ C.$  with decomposition. It is found in the root-bark of apple, pear, plum, cherry, and other fruit trees, which upon hydrolysis yields phloretin ( $C_{16}H_{14}O_5$ ) and grape-sugar; soluble in alcohol and hot water. (See *An Introduction to the Chemistry of Plant Products*, by Paul Haas and T. G. Hill (Longmans, Green and Co., London).)

**PHOLEDRINE SULPHATE** ( $C_{10}H_{15}ON)_2 \cdot H_2SO_4$ ) — A white amorphous solid, being the sulphate of  $\beta$ -methylamino-4-hydroxypropylbenzene; soluble in water, insoluble in alcohol, chloroform, and ether. Used in medicine to maintain the blood pressure during surgical operations.

**PHOSGENE** — See Carbonyl Chloride.

**PHOSPHATE ROCK** — A map of the phosphate deposits of the United States surveyed by 1915, including the fields of Montana, Idaho, Utah, and Wyoming, appears in *Mineral Resources of the United States* (U.S. Geological Survey), 1915, Part 2, 234. Analyses of 137 samples of phosphate rock from 34 countries and localities are given in *Ind. Eng. Chem.*, 24, 86 (1932). (See Calcium (Phosphate), Coprolites, Fertilizers, Phosphorite, Phosphorus, and Superphosphate.)

**PHOSPHATES** — See Calcium (Phosphate), and Phosphorus.

**PHOSPHATIC MANURES** — See Bones, Coprolites, Fertilizers, Phosphates, Superphosphate, and Slag.

**PHOSPHATIDES** — The International Union of Pure and Applied Chemistry has suggested the abandonment of this term and the substitution of the word "phospholipid" for lipids containing phosphorus, and "phosphoaminolipid" for those containing phosphorus nuclei and amino nitrogen. (See Brain Matter, and Glycerophosphoric Acid.)

**PHOSPHIDES** — See Phosphorus (Compounds).

**PHOSPHINE** — See Phosphorus (Compounds).

**PHOSPHINES (Organic)** — Feebly basic compounds prepared from phosphoretted hydrogen (phosphine) ( $PH_3$ ) by the substitution of hydrogen with alkyl radicals—for example, triethyl phosphine ( $P(C_2H_5)_3$ ). They correspond closely to the amines in composition.

**PHOSPHITES** — See Phosphorus (Compounds).

**PHOSPHOMOLYBDIC ACID** — See Phosphorus (Compounds).

**PHOSPHONIUM COMPOUNDS** — See Phosphorus (Compounds).

**PHOSPHOR BRONZE** — Copper-base alloys containing around 10 to 14 per cent. tin and 0.1 to 0.3 per cent. phosphorus with or without additions of lead and nickel. These alloys are known for their low coefficient of friction, making them suitable for bearings and gears. They can be employed for such applications where springiness, resistance to corrosion, and non-magnetic properties are desirable, as in instrument springs, and marine fittings. (See *Metals*, Vol. II, by H. Carpenter and J. M. Robertson (Oxford University Press) and other references under Physical Metallurgy.)

**PHOSPHORESCENCE** — See Light, Luminosity, Radium, and Zinc (Sulphide).

**PHOSPHORETTED HYDROGEN (Phosphine)** — See Phosphorus (Compounds).

**PHOSPHORIC ACIDS** — See Phosphorus (Compounds).

**PHOSPHORITE (Rock Phosphate of Calcium)** — Essentially tricalcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ). (See Phosphate Rock.)

### PHOSPHORUS-CONTAINING SUBSTANCES

#### CHART SHOWING PRINCIPAL INTER-RELATIONSHIPS

Arrangement Based on Valency and Reduction-Oxidation Properties

Arranged by the Editor.

Phosphine	Hypophosphorous Acid	Phosphorous Acid	Hypophosphoric Acid	Phosphoric Acid
$\text{PH}_3$	$\text{H}_3\text{PO}_2$	$\text{H}_3\text{PO}_3$ ortho $\text{H}_4\text{P}_2\text{O}_5$ pyro $\text{HPO}_3$ meta	$\text{H}_2\text{PO}_3$	$\text{H}_3\text{PO}_4$ ortho $\text{H}_4\text{P}_2\text{O}_7$ pyro $\text{HPO}_3$ meta
	Phosphorus P	Phosphorus Trioxide $\text{P}_2\text{O}_3$ Phosphorus Trichloride $\text{PCl}_3$	Phosphorus Tetroxide $\text{P}_2\text{O}_4$ Phosphorus Tetrachloride $\text{PCl}_4$	Phosphorus Pentoxide $\text{P}_2\text{O}_5$ Phosphorus Pentachloride $\text{PCl}_5$
Phosphine Comp. INORGANIC $\text{PH}_4\text{I}$	Hypophosphites	Phosphites INORGANIC Ortho, pyro, meta Normal, acid ORGANIC Phosphinic acids $\text{CH}_3\text{PO}(\text{OH})_2$ $(\text{CH}_3)_2\text{POOH}$ Phosphine oxides $(\text{CH}_3)_3\text{PO}$	Hypophosphates	Phosphates INORGANIC Ortho, pyro, meta Normal, acid ORGANIC $(\text{C}_6\text{H}_5\text{O})_2\text{PO}$
$\text{CH}_3\text{PH}_2$ $(\text{CH}_3)_2\text{PH}$  $(\text{CH}_3)_3\text{P}$ $(\text{CH}_3)_4\text{PI}$	Phosphobenzene $\text{C}_6\text{H}_5\text{P} : \text{PC}_6\text{H}_5$			Phosphoproteins

"Phosphorus is one of the most remarkable of the many remarkable substances known to the chemist" (T. E. Thorpe).

**PHOSPHORUS (P) and its Compounds** — Atomic weight 30.98. See Elements for other data; and also accompanying Chart. Phosphorus does not occur in nature in its free state, but abounds in combination as calcium phosphate in the seeds of plants and in soils, its presence in the latter being derived from the disintegration of rocks. Plants require phosphates as an essential to their proper growth and development, and the animal kingdom obtains its supply in turn from vegetable life. ("The Rôle of Phosphorus in Agriculture" is the subject of an article by E. Vanstone (*J.S.C.I.*, 45, 78 T (1926)).) Phosphorus in various combinations is a constituent of many animal tissues, including brain matter, while the bones owe their rigidity to calcium phosphate, which makes up 60 per cent. of their substance. Bone ash, indeed, consisting as it does, in the main, of that substance, is one of the important sources of phosphorus. (See Bones.) In various combinations as phosphate, it is present in the minerals *sombrerite* ( $\text{Ca}_3(\text{PO}_4)_2$ ), *apatite* ( $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaF}_2$ ), *wavellite* ( $4\text{AlPO}_4 \cdot \text{Al}_2(\text{OH})_6 \cdot 9\text{H}_2\text{O}$ ), also in Gafsa phosphate, "Ephos," "Naura," "Buccaneer," and Coprolites. (See Coprolites; and Calcium (Phosphate) for economic data.)

Large deposits of rock phosphates are found in Tunisia, Algiers, Morocco, Egypt, Esthonia, the Somme (France), Montana, Idaho, Utah, Wyoming, Florida, South Carolina, the Pacific Islands, Hokaidaito

Islands (Japan), etc. Naura phosphate (New Zealand) contains about 85.28 per cent. tricalcium phosphate, and North African about 63.35 per cent. (See Phosphate Rock.)

Phosphorus is made from bone ash or sombreroite (1) by treatment with sulphuric acid of sp. gr. about 1.5, when the following interaction takes place:  $\text{Ca}_3(\text{PO}_4)_2 + 3\text{H}_2\text{SO}_4 = 3\text{CaSO}_4 + 2\text{H}_3\text{PO}_4$ , insoluble calcium sulphate and a solution of phosphoric acid being obtained. After filtration of the mixture, the liquid filtrate is concentrated by evaporation and yields the acid in crystalline form of deliquescent nature. From the acid so prepared, phosphorus may be obtained by mixing it with powdered charcoal, heating, and subsequent distillation; at first, the phosphoric acid is broken up into water and metaphosphoric acid as follows,  $\text{H}_3\text{PO}_4 = \text{H}_2\text{O} + \text{HPO}_3$ ; and at a later stage there is a further change by which this acid is decomposed ( $4\text{HPO}_3 + 12\text{C} = 12\text{CO} + 2\text{H}_2 + 4\text{P}$ ), the phosphorus being condensed in dark yellow drops under water, in which it subsequently solidifies. It is now chiefly produced (2) by the less wasteful and more economical "Readman" process in which silica takes the place of sulphuric acid:  $\text{Ca}_3(\text{PO}_4)_2 + 5\text{C} + 3\text{SiO}_2 = 3\text{CaSiO}_3 + 5\text{CO} + 2\text{P}$ . The calcium silicate is drawn off as a molten slag from the electric furnace in which the reaction takes place, and the carbon monoxide and phosphorus are removed as gas and vapour, respectively. The phosphorus is condensed under water and collected.

In the pure state, phosphorus is a slightly yellowish-white, semi-transparent, wax-like substance, which takes fire when warmed and exposed to the air, so that it has to be kept submerged in water. (See Ozone.) In its ordinary form it is very poisonous, has a sp. gr. of 1.82, and is soluble in carbon disulphide, from which it may be obtained upon evaporation in the form of colourless crystals. It may also be sublimated *in vacuo* and obtained in beautiful crystals. The glow of phosphorus exhibited during its slow oxidation, its inhibition, and some other features have been studied by H. J. Emeléus.

Phosphorus is allotropic, that is to say, it can be made to assume more forms than its ordinary almost colourless waxy one. When heated to between 240° and 250° C. out of contact with the air, it passes into a red form, which has a sp. gr. of 2.2, and, unlike the ordinary yellow phosphorus, is not luminous in the dark, and is not poisonous. A mixture of the two forms is produced by the rapid cooling of phosphorus vapour, but only the yellow form by slow cooling. A black form resulting from long exposure to light is changed into the scarlet form on being heated to 575° C., and the melting-point of the red variety has been determined as  $592.5^\circ \pm 0.5^\circ \text{C}$ .

Phosphorus is largely used in match-making, the preparation of rat-poison, the manufacture of phosphor bronze, the manufacture of phosphoric acid and phosphates.

For Phosphate Rock Production Data, see Calcium, and Fertilizers.

It forms several compounds with hydrogen, the better known being **hydrogen phosphide** (phosphine or phosphoretted hydrogen) ( $\text{PH}_3$ ), which is formed when red phosphorus is gently heated in a current of hydrogen gas; also by the action of a hot solution of sodium hydroxide

on phosphorus, or by the action of water upon calcium phosphide. This is a colourless, highly poisonous gas, soluble in alcohol and ether, of offensive garlic-like odour, and as formed spontaneously takes fire at a temperature below that of boiling water.

Calcium phosphide is employed in the construction of drain-testers, and the action of water upon that substance finds practical employment also in the marine appliance known as Holmes's signal. In the case of the drain-testers, the distinctive odour of the gas enables the operator to detect leakages in drains, whilst in the case of Holmes's signal, the phosphine ignites and burns, giving a considerable illumination.

**Hypophosphorous Acid** ( $\text{H}_3\text{PO}_2$ ) is a white crystalline body (m.p.  $26.5^\circ\text{C}$ .), obtained by decomposing its barium salt ( $\text{Ba}(\text{H}_2\text{PO}_2)_2$ ) with sulphuric acid, the barium compound in its turn being prepared by boiling phosphorus in a solution of barium hydroxide (as described above in the case of sodium hydroxide, where sodium hypophosphite is formed simultaneously with hydrogen phosphide).

Several of the hypophosphites, including the potassium, sodium, and calcium salts, are used in medicine.

**Phosphoric Acid (Orthophosphoric Acid)** ( $\text{H}_3\text{PO}_4$ ) is put up in various forms, such as liquid containing 66 to 85 per cent.  $\text{H}_3\text{PO}_4$ , paste containing 40 to 50 per cent., crystals of m.p.  $42^\circ\text{C}$ ., and acids of lower water content (partially dehydrated) than  $\text{H}_3\text{PO}_4$ .

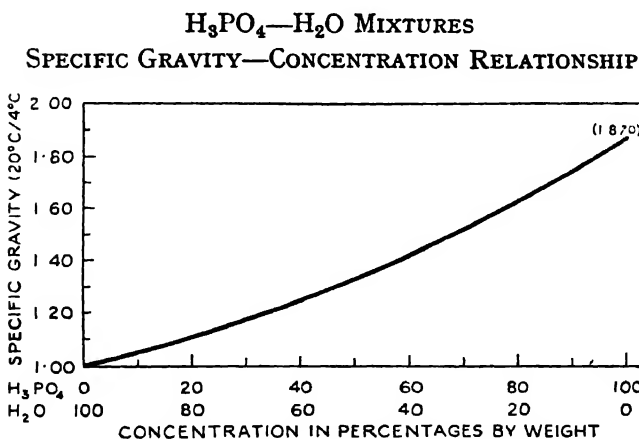
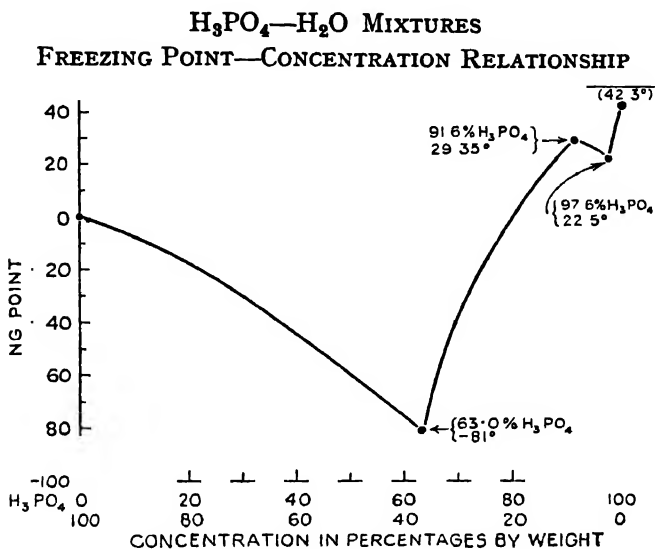
Phosphates are obtained by neutralization with alkali to the required point and crystallization. The acid finds employment in defecating sugar, and in the glass and mineral water industries, etc., and can be used for making monocalcium phosphate and other fertilizers of greater concentration than ordinary "superphosphate," also disodium phosphate.

In the "Liljenroth" process, phosphate rock is reduced with coke and some silicate in an electrical furnace, giving phosphorus, the vapour of which together with steam is passed over a catalyst at about  $1,000^\circ\text{C}$ ., hydrogen being set free as a by-product. This can be used for ammonia synthesis and the ammonia combined with the phosphoric acid to form ammonium phosphate.

Phosphoric acid, in the form of soluble phosphates, enters into the composition of many medicines, such as chemical foods and nerve stimulants: phosphates are also used in the dyeing and bleaching trades, the fireproofing of woods, and in sugar-refining. The natural phosphates, with or without treatment, are largely used in agriculture as fertilizers, and it is claimed that rock phosphates give equal results to those secured from the high citric acid-soluble types of basic slag.

The availability of any particular phosphate depends in some degree upon the manner and the extent to which it takes part in the various soil reactions—that is to say, their fertilizing values must bear some definite relation to their relative solubility in soil solution. (See "Phosphorus and Phosphates," in *Chem. Eng.*, Aug., 1948; Oct., 1948; W. H. Waageman's *Phosphoric Acid, Phosphates and Phosphate Fertilizers* (Reinhold Publishing Corp., New York); and Slag.)

**Metaphosphoric Acid (Glacial Phosphoric Acid)** ( $\text{HPO}_3$ ) is a highly deliquescent glacial compound resulting from the deliquescence of phosphorus pentoxide, and can be obtained by heating orthophosphoric acid to redness, by which it loses a molecule of water:  $\text{H}_3\text{PO}_4 - \text{H}_2\text{O} = \text{HPO}_3$ . At higher temperatures it sublimes (the oxide is not formed). It is used in pharmacy and medicine.



**Pyrophosphoric Acid** ( $\text{H}_4\text{P}_2\text{O}_7$ ) is a white crystalline body, soluble in water, which can be prepared in a number of ways, as, for example, by heating the ortho-acid to  $213^\circ \text{C}$ ., when two molecules lose a molecule of water, yielding the pyro-acid:  $2\text{H}_3\text{PO}_4 - \text{H}_2\text{O} = \text{H}_4\text{P}_2\text{O}_7$ .

**Phosphorous Acid** ( $\text{H}_3\text{PO}_3$ ) is a white crystalline body (m.p.  $74^\circ \text{C}.$ ), formed by dissolving phosphorous oxide in water or by the action of water upon phosphorus trichloride:  $\text{PCl}_3 + 3\text{H}_2\text{O} = 3\text{HCl} + \text{H}_3\text{PO}_3$ . It is dibasic, and forms two classes of salts (phosphites and acid phosphites).

Two **perphosphoric acids** are known to exist, namely,  $\text{H}_3\text{PO}_5$  and  $\text{H}_4\text{P}_2\text{O}_8$ , the former being prepared by the action of 30 per cent. hydrogen peroxide solution on phosphorus pentoxide, and the latter by the same reagent acting on syrupy phosphoric acid.

All these acids and a number of their salts are used industrially.

**Hypophosphoric Acid** ( $\text{H}_4\text{P}_2\text{O}_6$ ) is stated to be formed by oxidation of red phosphorus with alkaline permanganate or hydrogen peroxide, the sodium salt being represented by  $\text{NaHPO}_2$ .

There are a number of **oxides** of phosphorus, of which the more important are the trioxide and the pentoxide.

**Phosphorus Trioxide** ( $\text{P}_2\text{O}_3$ ), a white, non-crystalline powder, is formed by burning phosphorus in a limited current of dry air; m.p.  $23^\circ \text{C}.$

**Phosphorus Pentoxide** ( $\text{P}_2\text{O}_5$ ) is formed when phosphorus is burned in excess of air or oxygen, and is a white sublimable powder (method of purification), used as a dehydrating agent (having a great affinity for water), also in sugar-refining.

**Phosphomolybdic Acid** ( $\text{H}_3\text{PO}_4 \cdot 12\text{MoO}_3$ ) — A yellow, crystalline substance soluble in water, used chemically as a reagent in the examination and preparation of alkaloids.

**Phosphorus Trichloride** ( $\text{PCl}_3$ ) is a colourless, fuming liquid, and the **pentachloride** ( $\text{PCl}_5$ ) is a yellow, crystalline body, both of which are made by the action of chlorine upon phosphorus, and are used as chlorinating agents; both are soluble in carbon disulphide.

Other compounds of phosphorus (salts of phosphine, **phosphonium salts**) include phosphonium chloride ( $\text{PH}_4\text{Cl}$ ), phosphonium bromide ( $\text{PH}_4\text{Br}$ ), phosphonium iodide ( $\text{PH}_4\text{I}$ ) (all of which are crystalline bodies); and two **fluorides** ( $\text{PF}_3$  and  $\text{PF}_5$ ), and two **bromides** ( $\text{PBr}_3$  and  $\text{PBr}_5$ ).

**PHOSPHORYL** — The trivalent radical:  $\text{P}:\text{O}$ , as it exists in combinations such as phosphoryl chloride ( $\text{POCl}_3$ )—a colourless, fuming liquid formed by the action of water upon phosphorus pentachloride, etc.

**PHOTOCATALYSIS and PHOTOSYNTHESIS** — A process in which a reaction proceeds due to the presence of light and a catalyst.

Photosynthesis is the photocatalytic process by which green plants convert carbon dioxide into organic matter. The primary products formed are the carbohydrates, glucose, fructose, and starch. From these compounds and their metabolic products all other organic compounds in plants are formed. In all plants the process takes place in cells containing the chlorophyll pigments. These pigments are found in the chloroplasts of higher plants.

A characteristic of photosynthesis in higher plants is the fact that

oxygen is given off as an end-product of the reaction. Experiment with heavy oxygen have proved that this oxygen arises from water and not from the carbon dioxide. This indicates that the hydrogen of water is used for the reduction of carbon dioxide. That this is undoubtedly so is shown by the fact that some photosynthesizing bacteria are known which require hydrogen sulphide and give off no oxygen. These bacteria therefore differ from higher plants by using hydrogen sulphide instead of water as a source of hydrogen.

The fixation of carbon dioxide is accomplished by certain organic acids, such as pyruvic and succinic, with the aid of enzymes. The carbon dioxide is fixed in the form of acid groups ( $-\text{COOH}$  groups). These compounds in which carbon dioxide has been fixed are then reduced by the hydrogen provided by water or other sources. How the required chemical energy is secured from light energy and the function of chlorophyll have not been explained.

See a comprehensive review of *Photosynthesis and Related Processes* (2 vol.), by E. I. Rabinowitch (Interscience Publishers, New York); and summaries by C. B. van Niel in *Chem. Eng. News*, **24**, 1363 (1946), and by H. Gaffron in *Currents in Biochemical Research*, 1946, 25 (Interscience Publishers, New York); *Photosynthesis*, by E. C. C. Baly (D. Van Nostrand Co., New York); *Photosynthesis in Plants*, by James Franck and W. E. Loomis (Iowa State College Press, Ames); *An Introduction to the Chemistry of Plant Products*, by Paul Haas and T. G. Hill (Longmans, Green and Co., London); and Plant Colouring Matters.

**PHOTOCHEMISTRY** — See Light (Photochemical Aspects), and Photocatalysis.

**PHOTOMETRY** treats of the measurement of the intensity of light. It consists of methods of physico-chemical analysis based upon the measurement of the amount of light absorbed by coloured solutions, called *colorimetry* or spectrophotometry, or by a white suspension, called *turbidimetry*, or of the amount of light scattered by a suspension, called *nephelometry*.

The concentration of a coloured solution can be determined directly by a colorimeter or a spectrometer. If the substance in solution is colourless it may often be converted into a coloured compound by a suitable chemical reaction or by using light of a different wave length in which the solution is coloured. For example, instead of using visible light for viewing the solution, X-rays or infra-red light may be used with the aid of a photographic film or a photoelectric or photronic cell.

In general, photometric principles are based upon Lambert's and Beer's laws of light transmission. When a beam of monochromatic light falls on a substance part of the light is reflected, part is absorbed, and part is transmitted. The laws of photometry deal with the relations between the intensity of incident light ( $I_0$ ) and the intensity of transmitted light ( $I_t$ ).

Lambert's laws state: (1) The amount of monochromatic light absorbed by a substance is proportional to the intensities of the transmitted ( $I_t$ ) and incident ( $I_o$ ) light, or  $\frac{I_t}{I_o} = A$ , where  $A$  is a constant dependent upon the substance, the wave length of the light, and the temperature, and is called the transmission coefficient. (2) The intensity of transmitted light decreases in geometric progression while the thickness of the film increases in arithmetic progression. This means that layers of the same thickness of a given substance absorb the same fraction of the incident light. If " $l$ " is the thickness of the transmission layer then  $I_t = I_o A^{-l}$ . In other words, the decrease in the intensity of light ( $dI$ ) as it passes through a thin film of thickness ( $dl$ ) is given by the equation:  $dI = -kI_o dl$ , where  $k$  is a proportionality constant or absorption coefficient. This equation can be expressed as  $I_t = I_o e^{-kl}$ , where  $e$  is the base of natural logarithms.

Beer's law states that the relation between the intensity of the transmitted light and the concentration of the substance in solution is the same as exists between light transmission ( $I_t$ ) and thickness of layer " $l$ ." Beer's law can be expressed as  $I_t = I_o A^{-C}$ , where  $C$  is the concentration of the substance in solution.

The primary advantage of photometric methods is that traces of substances can be detected and determined in a simple way and they are therefore suitable for micro-quantities. In general the accuracy of photometric methods are about 1 to 2 per cent.; however, improvements in instrumentation and methods may be expected to increase the accuracy.

There are many substances that do not follow Beer's and Lambert's laws. The variation can often be overcome by calibrating the instrument against known concentrations of the particular substance.

*References:* *Photometric Chemical Analysis*, by J. H. Yoe (John Wiley and Sons, New York); *Textbook of Quantitative Inorganic Analysis*, by Kolthoff and Sandell (Macmillan Co., New York); "Photoelectric Methods," by R. H. Müller (*Ind. Eng. Chem., Anal. Ed.*, **11**, 1 (1939)); "Spectrometric Methods," by S. E. Q. Ashley (*Ind. Eng. Chem., Anal. Ed.*, **11**, 72 (1939)).

**PHOTON** — Many facts connected with radiation are best explained by supposing that light consists of energy quanta, called photons, travelling with the velocity of  $3 \times 10^{10}$  centimetres per second. When light passes through slits or encounters obstacles which are small in comparison to the wave length of light it is essential to think of light in terms of wave motion. If the slits or obstacles are relatively large, the corpuscular concept of light is satisfactory. This dualism of wave and particle nature of light is generally accepted and is used in explaining the behaviour of subatomic phenomena.

The energy ( $E$ ) associated with a photon is dependent upon the frequency of the radiation ( $\nu$ ) and Planck's constant ( $h$ ) by the following equation  $E = h\nu$ . (See Energy.)

*References:* *Introduction to Modern Physics*, by Richtmeyer and

Kennard (McGraw-Hill Book Co., New York); *A Treatise on Light* by Houston (Longmans, Green and Co., New York); *Physical Optics*, by Wood (Macmillan Co., New York).

**PHOTOSYNTHESIS** — See Photocatalysis.

**"PHRENAZOL"** — See Leptazol.

**PHTHALEÏNS** — A group of triphenylmethane dyes, obtained by condensing phthalic anhydride with phenols. The best-known are phenolphthaleïn and fluoresceïn, while tetraiodophenolphthaleïn is important in medicine in X-ray diagnosis.

**PHTHALIC ACID** ( $C_6H_4(COOH)_2$ ) — A colourless crystalline substance, readily soluble in alcohol and ether, which is made commercially by oxidizing naphthalene with fuming sulphuric acid in the presence of a small quantity of mercury at  $220^\circ$  to  $230^\circ$  C., and by catalytic oxidation of naphthalene vapour mixed with air passed over heated vanadium pentoxide (product is mainly phthalic anhydride). The *ortho*-acid melts at  $207^\circ$  C., and is used in the synthetic production of indigo, etc.; the *meta*-acid is known as isophthalic acid; and the *para*- as terephthalic acid.

**PHTHALIC ANHYDRIDE** ( $C_6H_4(CO)_2O$ ) — A white crystalline body, m.p.  $131^\circ$  C., used in preparing eosin dyes, etc.; soluble in alcohol, and obtained by distillation of phthalic acid, or warming the acid with acetyl chloride, etc. It is commercially prepared by oxidation of naphthalene with concentrated sulphuric acid containing mercury sulphate, or oxide or metal, which acts catalytically, the sulphur dioxide formed in the process being reconverted into sulphuric acid by air; and vanadium catalysts are effective. Synthetic resins can be made from phthalic anhydride condensed with glycerol. (See Skeen, *Chem. Eng. News*, **26**, 2958 (1948).)

**PHTHALIMIDE** — See Imides.

**PHTHALYLSULPHATHIAZOLE** ("Sulfathalidine," "Thalazole," "Thalinstatin") ( $C_{17}H_{13}O_5N_3S_2$ ) — A white or slightly off-white, odourless, tasteless crystalline compound, namely, 2-(*p*-phthalylaminobenzene-sulphonamido)thiazole,



prepared by condensing sulphathiazole with phthalic anhydride; almost insoluble in water; sparingly soluble in alcohol and acetone; insoluble in ether and chloroform; soluble in solutions of alkali hydroxides and carbonates; it chars at about  $260^\circ$  C. without melting. It is almost entirely unabsorbed on oral administration and is used for the treatment of local intestinal infections such as bacillary dysentery. It is about twice as active as succinylsulphathiazole which is used for the same purposes. (See Sulphanilamide.)

**"PHYSEPTONE"** — See Amidone.

**PHYSICAL CHEMISTRY** — Physical or theoretical chemistry is that branch of the science that deals with "the nature of the mechanism of chemical changes (Friend)," and its purpose is "to know, to understand, and to use the laws of chemistry and physics (Getman and Daniels)."

*References* : *A Treatise on Physical Chemistry*, by a group of physical chemists, edited by H. S. Taylor (D. Van Nostrand Co., New York); *Outlines of Theoretical Chemistry*, by F. H. Getman and F. Daniels (John Wiley and Sons, New York); *A System of Physical Chemistry*, by W. C. McC. Lewis (Longmans, Green and Co.); *Physico-Chemical Methods*, by J. Reilly and W. N. Rae (D. Van Nostrand Co., New York); *A Text-book of Physical Chemistry*, by J. Newton Friend (Charles Griffin and Co., London); *Theoretical and Experimental Physical Chemistry*, by Crocker and Matthews (J. and A. Churchill, London); *Physical and Inorganic Chemistry—Recent Advances in*, by A. W. Stewart (Longmans, Green and Co., London); *Recent Advances in Physical Chemistry*, by S. Glasstone (J. and A. Churchill, London); *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Co., Cleveland, Ohio); *Handbook of Chemistry*, by N. A. Lange (Handbook Publishers, Inc., Sandusky, Ohio); *Practical Physical Chemistry*, by A. Findlay (Longmans, Green and Co., London); *Fundamental Principles of Physical Chemistry*, by Carl F. Prutton and S. H. Maron (Macmillan Co., New York); also Atoms, Electricity, Elements, Heat, Light, Matter, and Molecules.

**PHYSICAL CONSTANTS** — See Constants.

**PHYSICAL METALLURGY** — A division of metallurgy dealing with the applications of chemical and physical knowledge to the melting, alloying, refining, casting, fabrication, heat treatment, and mechanical testing of metals and alloys.

*References* : *The Principles of Physical Metallurgy*, by G. E. Doan (McGraw-Hill Book Co., New York); *The Principles of Physical Metallurgy*, by F. L. Coonan (Harper's, New York); *Practical Metallurgy*, by G. Sachs and K. R. Van Horn (American Society for Metals, Cleveland, Ohio); *Metals*, Vols. I and II, by H. Carpenter and J. H. Robertson (Oxford University Press); *Essential Metallurgy for Engineers*, by A. C. Vivian (Sir Isaac Pitman and Sons, London); *The Mechanical Testing of Metals and Alloys*, by P. F. Foster (Sir Isaac Pitman and Sons, London); *Structure and Properties of Alloys*, by R. M. Brick and A. Phillips (McGraw-Hill Book Co., New York); *Principles of Metallography*, by R. S. Williams and V. O. Homerberg (McGraw-Hill Book Co., New York); *The Metallography and Heat Treatment of Iron and Steel*, by A. Sauver (McGraw-Hill Book Co., New York); *The Science of Metals*, by Z. Jeffries and R. S. Archer (McGraw-Hill Book Co., New York); *Introduction to Physical Metallurgy*, by W. Rosenhain (Constable and Co., London); *Metallurgy*, by C. G. Johnson (American Technical Society, Chicago); *An Introduction to Physical Metallurgy*, by L. R. Van Wert (McGraw-Hill Book Co., New York); and *Ferrous Metallurgical Design*, by J. H. Hollomon and L. D. Jaffe (John Wiley and Sons, New York).

**PHYSIOLOGICAL CHEMISTRY** — See Biochemistry.

**PHYSOSTIGMINE (Eserine)** ( $C_{15}H_{21}O_2N_3$ ) — A crystalline alkaloid obtained from the ripe seeds of *Physostigma venenosum*; m.p.  $105^\circ$  to  $106^\circ$  C.; insoluble in water but soluble in alcohol, ether, and chloroform. It is used in medicine in the form of its sulphate or salicylate, the latter being preferred because of its greater stability; aqueous solutions turn pink on exposure to light and air. Physostigmine antagonizes the action of atropine on the eye, causing contraction of the pupil. (See Calabar Bean.)

**PHYTOSTEROLS** — Sterols obtained from vegetable sources. (See Sterols.)

**PIASSAVA** — A fibre derived from the leaf stalks of the two palms (*Raphia vinifera* and *Raphia Gaertneri*) of Sierra Leone (Southern and Central Provinces); used in making coarse brooms. (See Raphia.)

**PICHURIM BEANS** (*Fabæ pichurim minores*, from *Ocotea pichura minor*, Martius) yield upon distillation with water a yellow oil with an odour like that of bay and sassafras oils, containing terpenes and a camphor, together with lauric acid. The Brazilian beans yield 2.1 per cent. oil of sp. gr. 1.0538, acid v. 9.7, and ester value 4.6.

**PICKLING** — See Galvanizing, and Rustless Iron.

**PICOLINES** ( $C_5H_4N(CH_3)$ ) — Methylpyridines (three) contained in bone oil and coal tar.

**PICRAMIC ACID (Dinitroaminophenol)** ( $C_6H_2(OH)(I)(NH_2)(2)(NO_2)_2(4,6)$ ) — A red, crystalline substance, soluble in alcohol and ether, which melts at  $169^\circ$  C., and is used in azo-dyestuffs.

**PICRIC ACID (Trinitrophenol)** ( $C_6H_2(OH)(I)(NO_2)_3(2,4,6)$ ) — A poisonous, lemon-coloured, crystalline substance (m.p.  $122^\circ$  C.), largely used as an explosive and as a yellow dye for silk and wool; prepared by the nitration of phenol in the presence of sulphuric acid at  $100^\circ$  C.; by the simultaneous nitration and oxidation of benzene by nitric acid in the presence of mercuric nitrate as a catalyst; and by the nitration of 2,4-dinitrophenol, which is made from chlorophenol by nitration and subsequent hydrolysis.

Picric acid explodes with violence when struck or when heated to above  $300^\circ$  C., is soluble in alcohol and sparingly soluble in water, to which it gives a deep yellow colour. Its melting temperature is reported to be an objection to its use as a high explosive; moreover, on solidifying from a melted state cavities are formed. (See Explosives.)

Picric acid is of great value in the identification and purification of organic compounds, as a very large number of them form characteristic picrates, which are usually crystalline solids of sharp melting points. Not only bases but a great variety of different types of compound behave in this manner, even hydrocarbons, such as naphthalene. Picrates are usually easily prepared, generally by simply mixing hot alcoholic solutions of the substance and of picric acid, and allowing to cool.

**PICROCROCIN** — See Glycosides.

**PICROTOXIN (Cocculin)** ( $C_{30}H_{34}O_{13}$ ) — A crystalline glycoside obtained from the seed of *Anamirta paniculata*; sparingly soluble in water; soluble in alcohol; sparingly soluble in ether and chloroform; m.p.  $198^{\circ}$  to  $200^{\circ}$  C. Picrotoxin has a stimulant action on the medulla and is used in medicine as a stimulant in cases of barbiturate and morphine poisoning. In larger doses it acts as a powerful convulsive poison. (See *Cocculus Indicus*.)

**PICUL BALE** — Approximately  $132\frac{1}{4}$  pounds of raw silk.

**PIEZOMETER** — Appliance for determining compressibilities of substances.

**PIDGEON PROCESS** — See Magnesium.

**PIGMENTS** — The pigment, or solid part of paint, consists of finely divided material chosen to give the desired colour and surface. The pigment must have good "hiding" powers and may be a white solid such as white lead, zinc oxide, lithopone, titanium dioxide, barium sulphate, calcium sulphate, and magnesium silicate, either alone or mixed with each other. The pigment also may be a coloured compound such as red lead, red iron oxide, green chromium oxide, prussian blue, carbon black, cobalt blue, and chrome yellow. Coloured pigments are also prepared by precipitating a colloidal compound in the presence of an organic dye of the desired colour. The colour of the dye is adsorbed by the precipitate and is called a "lake."

See A. P. Laurie on "Identification of Pigments used in Painting at Different Periods" (*Analyst*, **55**, 162 (1930)); *Artificial Organic Pigments*, by C. A. Curtis (Pitman and Sons, London); *The Manufacture of Lakes and Precipitated Pigments*, by A. W. C. Harrison (Leonard Hill, London); also Carbon, Colour, Colouring Matters, Dyes, Lakes, Iron Oxides, Mineral Black, and Paints.

**PILCHARD OIL** — See Fish Oils.

**PILE** — See Reactor (term preferred by the Atomic Energy Commission).

**PILI NUT OIL**, from the seeds of *Canarium oratum*, is edible and composed of glycerides in proportions of oleic 59.6, palmitic 38.2, and stearic 1.8. Its sp. gr. at  $30^{\circ}$  C. is 0.907; i.v. (Hübl), 55.9; sap. v., 197.4; and acid value, 1.42.

**PILOCARPINE** ( $C_{11}H_{16}O_2N_2$ ) — A poisonous alkaloid obtained from the leaves of *Pilocarpus microphyllus*; a shrub indigenous to Brazil. It is a colourless or slightly yellow viscid liquid or crystalline substance, m.p.  $34^{\circ}$  C., freely soluble in water, alcohol, and chloroform. It is used in medicine in the form of its nitrate, which is a colourless crystalline solid; soluble in water; m.p.  $174^{\circ}$  to  $178^{\circ}$  C. The main use is in ophthalmology to produce contraction of the pupil of the eye and reduce the intra-ocular tension in glaucoma. Its activity is about one-half that of physostigmine. Pilocarpine is a common constituent of hair tonics but there is no evidence of its favouring the growth of hair.

**PILOT PLANT** — Any small plant used to test or develop a new manufacturing process (see Process Development). A pilot plant need not reproduce in miniature every operation in the proposed large-scale plant, but only such operations as are novel; its chief function is to furnish design data that cannot be obtained in any other way. The capacity or throughput of a pilot plant unit is generally between 1/100 and 1/10 that of the corresponding large-scale unit. Elaborate instrumentation is often needed, and this may be the most costly item.

The modern tendency in process development is to reduce the amount of pilot plant experimentation as more is learnt about the theory of chemical plant design. Occasionally the pilot plant stage is omitted altogether, a step that may be economically justified where a new process is entirely composed of standard unit operations.

The theory of pilot plant design and the interpretation of results, so far as it exists, is based upon the Principle of Similarity.

*References:* (1) General, *Ind. Eng. Chem.* (Symposium), **37**, 412 (1945). (2) Theoretical, R. Edgeworth Johnstone in *Trans. Inst. Chem. Engrs. (London)*, **17**, 129 (1939); D. M. Hurt in *Ind. Eng. Chem.*, **35**, 522 (1943).

**PIMARIC ACID** — See Abietic Acid.

**PIMELITE** — Native green nickeliferous silicate.

**PIMENTO OIL (Allspice Oil)** — A yellow or yellowish-red, volatile oil, distilled from the fruit of *Pimenta officinalis*, containing about 60 to 95 per cent. of eugenol and a sesquiterpene; soluble in alcohol and ether; sp. gr. 1.035 to 1.057 at 15° C.; ref. ind. 1.500 to 1.536 at 20° C.; opt. rot. 0° to -5°. Pimento oil darkens and thickens on exposure to air and resembles oil of cloves in odour. It is used in perfumery, and as a flavouring agent.

**"PINACYANOL"** — A dyestuff that sensitizes photographic plates far into the red region of the spectrum.

**"PINA-KRYPTOL"** — A mixture of a colourless compound with a small proportion of the green dye "pina-kryptol green," used as a photographic desensitizer.

**"PINAVERDOL"** — An isocyanine dyestuff used for sensitizing photographic plates through the green and well into the red region of the spectrum.

**PINCHBECK** — An alloy gold-like in appearance consisting of copper and zinc in varying proportions, about 1 part zinc and 8 parts copper.

**PINE OIL** — A name variously used but originally applied to the turpentine-like oils obtained from pine and fir trees, particularly those from the seeds and needles. They vary considerably in their odours, drying properties, and rotatory powers.

Pine oil of commerce is a crude turpentine obtained in the United States by the destructive distillation of pine wood (now practically out of use) and the so-called steam or steam and solvent method. The "light wood" used is obtained from *Pinus palustris*, *P. heterophylla*,

and *P. echinata*, although any wood rich in resinous material can be used. The oil contains terpenes, terpineol, and a number of other substances. The product obtained by the steam method has a sp. gr. of from 0.920 to 0.945 at 20° C., and ref. ind. 1.4820 to 1.4870 at 20° C. (See Turpentine.)

**Pumilio Pine Oil** — The volatile oil distilled from the fresh leaves of *Pinus pumilio*, occurring as a colourless or faintly yellow liquid having a pleasant balsamic odour; soluble in alcohol and ether; sp. gr. 0.865 to 0.873 at 15° C.; opt. rot.  $-6^{\circ}$  to  $-15^{\circ}$ ; ref. ind. 1.470 to 1.480 at 20° C. It contains bornyl acetate with *l*-pinene, *l*-phellandrene, sylvestrene, dipentene, and cadinene.

**"Huon" Pine Oil** is a yellow to brown oil produced in Tasmania by steam distillation of chips and sawdust of *Dacrydium franklini*, containing about 90 per cent. of methyleugenol; sp. gr. about 1.048.

**PINE-CONE OIL** — See Turpentine.

**PINE-LEAF OIL** — See Turpentine.

**PINE-NEEDLE OIL** — See Pine Oil.

**PINE TAR OIL** — The distillate of pine tar, boiling between 160° and 170° C. and consisting of a colourless, highly refractive liquid, darkening to a reddish-brown colour on keeping. It is soluble in turpentine, and is sometimes used in ore concentration by the flotation process.

**PINENE (Alpha-Pinene)** ( $C_{10}H_{16}$ ) — The most abundant dicyclic terpene, obtained mainly from oil of turpentine. From it may be obtained dipentene, terpineol, terpin, terpin hydrate, and camphor. Among its oxidation products are pinonic acid, pinic acid, and norpinic acid (2,2-dimethyl-1,3-cyclobutane dicarboxylic acid). Pinene has sp. gr. 0.878 and b.p. 156° C. (See Hydrocarbons (Terpenes).)

**PINKING** — See Motor Spirit.

**PINOLINE** — See Rosin Spirit.

**PIPECLAY** — A peculiar variety of clay found in Cornwall, Dorsetshire, and Devonshire, used for making tobacco pipes, certain kinds of pottery, and for whitening soldiers' belts, etc.

**PIPER (Piper Nigrum)** — See Pepper Oil.

**PIPERIDINE** ( $(CH_2(CH_2)_4NH)$ ) — A colourless, liquid base, with an

odour resembling pepper, in which it is found as the substituted amide of piperic acid—the alkaloid piperine. It may be prepared by the reduction of pyridine with sodium and alcohol. It boils at 106° C., is miscible with water and alcohol, and yields crystalline salts.

**PIPERINE** ( $C_{17}H_{19}O_3N$ ) — A crystalline alkaloid, of m.p. 129° C., occurring in black pepper to the extent of from 5 to 9 per cent.; also in oil of cubebs. It is hydrolysed by the action of alcoholic sodium or potassium hydroxide to piperidine and piperic acid. Pepper owes its taste to the piperine content. (See Piperidine.)

**PIPERITONE** ( $C_{10}H_{16}O$ ) — A ketonic constituent of the eucalyptus oils yielded by the *Eucalyptus piperita* and *E. dives*, and present in some to the extent of from 40 to 50 per cent. Pure *l*-piperitone may be obtained from these oils by treatment with a concentrated solution of resorcinol or sodium salicylate, followed by steam distillation (see S. Kimura, *B.C.A.*, A, 1930, 1294). Both menthol and thymol can be prepared from it by processes of reduction and oxidation respectively. *d*-Piperitone is also one of the main constituents of the essential oil from *Andropogon Iwarancusa* (Jones), a grass which grows in the Himalayas and Assam. Optically active piperitone undergoes racemization during formation of most of its common derivatives. (See Thymol.)

**PIPERONAL (Heliotropin)** ( $CH_2O_2 : C_8H_8.CHO$ ) — Piperonal is a perfume material, occurring in the heliotrope, and can be synthesized from safrole of sassafras oil.

**PIPETTES** are glass tubes, with or without bulbs, used for transferring given measures of liquid from one vessel to another, and are made to deliver definite quantities by the aid of marks graduated thereon. Pipettes are also used, in analysing gases, to store gas samples and allow of their transfer as desired.

**PITCH** is a generic name applied to a number of products more or less identical in character but variously produced.

**Gas-Tar Pitch or Coal-Tar Pitch** is the residue left in the retorts from the distillation of gas tar, of which about 550,000 tons are annually produced in the United Kingdom. It finds use in roofing, as a binding material in the making of briquettes and joining up wooden road-paving blocks, also in making a black, coarse varnish and for insulating applications, etc. Water-gas pitch differs from horizontal retort pitch in having a lower "free carbon" content. The qualities which make pitch more suitable for fuel briquetting have been studied by the Fuel Research Board, and it has been found that the viscosity decreases steadily with increase of temperature, and that it is increased by melting and again cooling.

Workers in the tar and pitch industries in Britain are more or less subject to epitheliomatous cancer, while in France there is comparative immunity, but to what extent this depends upon differences in the chemical constitution of the several pitches or the heavy oils and residues of tar distillation is not known.

"Cellactite" is the name given to a product made from ordinary hard pitch, which, with an equal weight of water, is fluid, and said to have great penetrative and covering power very suitable for mixing with asbestos or cellulose fibre prior to felting, etc.

**Rosin Pitch** is that left behind from the destructive distillation of rosin, and can be used for the same purposes as coal-tar pitch.

There are also varieties of pitch left behind from the distillation of shale, wood, petroleum oils, and blast-furnace oil.

**Stearine Pitch**, obtained as a residual from the distillation of fatty

acids, is hard, bright, has a peculiar odour, and an iodine value of 50 to 70, which distinguishes it from petroleum and asphalt pitches. It is used in the manufacture of black enamels and flooring materials. (See Stearin.)

**Wool Pitch** is the residue left in the still after distillation of wool-fat, the process being generally finished at between 315° and 371° C. It is odourless and is made in several forms—liquid to medium-hard—the harder variety melting at about 38° C. It is chiefly used for making hot neck greases for tinplate roll mills; also for insulating purposes and in paper manufacturing.

**Burgundy Pitch** is not a "pitch" in the same sense. (See Burgundy Pitch.)

The various classes of pitch are different in some respects, but consist in the main of hydrocarbons, and all of them find employment particularly in the preparation of waterproofing materials. The Metroplastimeter is a device for taking measurements of the consistency of pitch at ordinary temperatures. (See Briquetting, and Tar.)

**PITCH BINDER** — See "Prodorite."

**PITCHBLENDE (Uraninite)** ( $\text{UO}, \text{U}_2\text{O}_3$ ) — A mineral of crystal system No. 1, and sp. gr. 6·4 to 9·7; used as a source of helium, radium, and uranium compounds. (See Uranium.)

**"PITOCIN"** — See Oxytocin.

**PLANCK'S CONSTANT** — See Photon.

**PLANKTON** — The drifting microscopic life of the sea.

**PLANT (Chemical)** — See Chemical Plant.

**PLANT COLOURING MATTERS** occur in the forms of so-called "plastid pigments" in the chloroplasts or granules of the cells. They include chlorophyll, carotene, etc. (which are intimately associated with the organized protoplasmic structure of plants), and the soluble "sap pigments," the latter class being divisible into two main classes, namely, (1) derivatives of flavone (flavonal), sometimes named anthoxanthenes, which are pale yellow or colourless when in faintly acid solution, but bright yellow in alkaline solution; and (2) the anthocyanins, which are red in acid solution, violet when neutral, and varying from dull red or reddish-brown to purple and blue when present in the form of alkaline salts in solution. It would appear from chemical investigations that the anthocyan (anthocyanin) pigments are reduction products of the yellow sap pigment, whilst botanical work points to the conclusion that these anthocyan pigments are present in plant life in positions that are known as the seat of oxidizing influences (oxydases): hence the hypothetical conception that pigmentation results from the action of oxydases on chromogens of colourless character.

The **anthocyanins** are glucosides of three parent anthocyanidins (or their methyl ethers) named pelargonidin, cyanidin, and delphinidin, whose hydrochlorides are formulated as  $\text{C}_{15}\text{H}_{11}\text{O}_5\text{Cl}$ ,  $\text{C}_{15}\text{H}_{11}\text{O}_6\text{Cl}$ , and

$C_{15}H_{11}O_7Cl$ . (See Delphinine.) In the formation of flower pigments, these glucosides are hydrolysed by enzymes of the emulsin type; the free chromogen is then oxidized by atmospheric oxygen activated by oxydases, and either dextrose, rhamnose, or galactose is formed, dextrose being the principal sugar. Pelargonidin, cyanidin, and a number of other allied substances have been synthesized.

The anthocyanins (anthocyanins) are said to contain similar nuclei, no matter how much they differ in colour, and the wide variation of tints is ascribed to slight differences in constitution which leave the main skeleton intact. Yeast decomposes anthocyanins with loss of sugar.

The colouring matter of the scarlet pelargonium known as "Scarlet Meteor" (*Pelargonium zonale*), and another variety, known as "James Kelway," occurs in the petals to the extent of 6.6 to 7.1 per cent. of the dry weight as an oxonium salt of the diglucoside of pelargonidin, namely, pelargonin (probably pelargonin tartrate), and was the first of the anthocyanin pigments obtained in crystalline form.

The anthocyanin of *Salvia coccinea* is named salvinin, and upon hydrolysis yields pelargonidin, dextrose, and malonic acid. That of the wallflower has been isolated, and the pigment of the polyanthus identified as a monoglucoside.

The red pigment of the young leaves of the grape-vine is said to be a free anthocyanidin, probably identical with cœnidin, the anthocyanidin of the purple grape (*Vitis vinifera*), although it may appear in a colourless modification termed a *leuco-anthocyanin*, in which it appears to be associated with another substance, possibly a carbohydrate, giving rise to anthocyanidin on treatment with strong acids. The same colouring matter occurs in the cactus, dahlia, and the pink cornflower, whereas blue cornflowers contain cyanin in potassium salt form. According to Anderson and Nabenhauer, the pigment in Clinton grapes (*Vitis riparia*) consists of a monoglucoside anthocyanin identical with that of the Norton and Concord grapes, the chloride ( $C_{23}H_{25}O_{12}Cl$ ) yielding by hydrolysis with hydrochloric acid one molecule each of glucose and anthocyanidin ( $C_{17}H_{15}O_7Cl$ ) of crystalline form, and having the same percentage and composition as cœnidin chloride, but differing from it in that it contains a lower percentage of methoxyl.

A red pigment known as "carajura" or "chica," prepared by Indians in Central America from a species of bush-rose, has been found by A. G. Perkin to contain a red crystalline substance named carajurin, having an anthocyanidin nucleus. The blue cornflower yields a pigment identical with that of the red rose, named cyanin, which gives a chloride of the composition  $C_{27}H_{31}O_{16}Cl$ , and upon heating this substance with a 20 per cent. solution of hydrochloric acid, it is hydrolysed into cyanidin ( $C_{15}H_{11}O_6Cl$ ) and glucose. The petals of the deep red rose "George Dickson" are stated to contain 10 per cent. of the anthocyan pigment cyanin, and the peel of the rosy apple is tinted with a pigment of the same class as that of the garden radish.

The green colouring matter, **chlorophyll**, present in the cells (chloroplasts) of the leaves and other parts of plants is only developed (so it has been alleged) when sulphur is present and when growth takes place

in the light. It is extractable from the leaves by acetone, while other solvents appear to separate it into two parts, which differ in their spectra and are known as A, which is described as a blue-black powder formulated as  $C_{55}H_{72}O_5N_4Mg$ , and B, a dark green powder formulated as  $C_{55}H_{70}O_6N_4Mg$ . There is a relationship between these several substances and the colouring matter of blood, as two of the pyrrole rings out of the three obtained from the reduction of chlorophyll are also obtained from hæmoglobin.

Fresh leaves are stated to contain about 2 grams of chlorophyll per kilogram, and a body named phytol, which has been synthesized, is an important item in its structure.

Chlorophyll is soluble in certain oils, alcohol, and ether, and is associated in the colouring materials of plants with carotene and xanthophyll, which is regarded as an oxidation product of carotene. Xanthophyll is soluble in ether at  $25^{\circ}C$ . to the extent of 952 milligrams per litre and oxidizes readily in that solution, but is stated to keep well in alcohol. Chlorophyll is the photocatalytic agent by means of which carbohydrates are formed in plants—possibly through the intermediate production of formaldehyde from carbon dioxide and water, the polymerization of that product into a kind of sugar, and, by the loss of water and condensation, the transformation of that sugar molecule into carbohydrates of the general formula  $(C_6H_{10}O_5)_n$ .

**Carotene (Carotin)** is an unsaturated hydrocarbon of the composition  $C_{40}H_{56}$ , which crystallizes in copper-coloured leaflets, absorbs oxygen readily from the air, and becomes converted into a colourless product. It is one of the most abundant of natural pigments, occurring with chlorophyll and xanthophyll in green leaves, and also in many flowers and fruits. In the animal organism it is present in milk, fat, and blood serum. Three isomerides, namely,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -carotene are found in carrot pigment, the difference between them being in the position of the double bonds. The solubility of carotene in absolute alcohol is stated to be 15.5 milligrams per litre, and in anhydrous ether 1,005 milligrams per litre, while 50 pounds of fresh carrots are said to yield 1.13 grams of pure carotene of m.p.  $174^{\circ}C$ . Submitted to five successive purifications, it is stated to have a m.p.  $184^{\circ}$  to  $185^{\circ}C$ . and to retain its vitamin activity.

Carotene confers immunity in growing rats against certain diseases which occur in them when vitamin A is absent from their diet, hence the value of carrots and green vegetables depends upon the presence in them of carotene, bearing in mind the value of these vegetables, together with eggs and butter, as sources of vitamin A. It is isomeric with another colouring matter named lycopene.

**Xanthophyll** and **fucoxanthin** are represented by the formulæ  $C_{40}H_{56}O_2$  and  $C_{40}H_{54}O_6$  respectively. According to Karrer, xanthophyll and carotene—both are yellow pigments of green leaves—may be separated by distribution between petroleum ether and 90 per cent. methanol, the xanthophyll collecting in the methanol layer and the carotene in the petroleum ether layer.

See Chlorophyll, Photosynthesis, and Plant Life.

**PLANT HORMONES** — Substances which act as regulators of physiological processes in plants: sometimes defined as “chemical messengers.” These compounds are effective in extremely small quantities, and serve to regulate the extent and direction of growth, root, and bud formation, flowering, and other processes. One group of the plant hormones is known as the *auxins*, and includes such chemical compounds as indoleacetic acid, naphthaleneacetic acid and 2,4-dichlorophenoxyacetic acid (“2,4-D”). These, as well as certain naturally occurring materials, serve to regulate growth. In excessive amounts some of them (especially “2,4-D”) will kill certain plant species, and are thus useful as herbicides. The *wound hormones* assist in the healing of wounds in plants, and include traumatic acid (1-decene-1,10-dicarboxylic acid). Other substances, such as ethylene, are classed as plant hormones by some workers, since they increase the rate of ripening of fruits. (See Boysen-Jensen, *Growth Hormones in Plants* (McGraw-Hill Book Co., New York); Mitchell and Marth, *Growth Regulators in Garden, Field and Orchard* (University of Chicago Press); Went and Thimann, *Phytohormones* (Macmillan, New York); and Herbicides.)

**PLANT LIFE** — Green plants transform the raw materials available in nature—inorganic chemicals, carbon dioxide, and water—into the more complex organic compounds which serve as food for the animal kingdom. This transformation is an elaborate process, and many of the intermediate steps are still not understood. The process of photosynthesis, whereby carbon dioxide and water are condensed into carbohydrates, is probably one of the most important reactions in nature, since it is the basis for all naturally occurring organic matter.

In addition to the carbohydrates, plants elaborate the many other food essentials required by animals. Inorganic nitrogen in nitrates and ammonia is combined with the hydrocarbon nuclei to form amino-acids, and from them, the proteins. Many plants, particularly the legumes, possess the ability to fix atmospheric nitrogen by means of symbiotic bacteria, and are thus largely independent of nitrogen compounds in the soil. Fats, the energy-producing foods for animals, are synthesized by plants, and seeds of various kinds constitute a most important source of these essential dietary constituents.

Many other substances essential to animal economy are produced solely by plants. The accessory factors, the vitamins, are synthesized in large quantities by various plant species, while in some cases animals are without this ability. Even the framework of the animal body, the skeleton, is derived from the minerals of the soil through the plant as an intermediate agency.

Plants are important to animals, not only as producers of the basic food materials, but also as a means of maintaining the constant composition of the atmosphere. The assimilating of carbon dioxide and elimination of oxygen in the photosynthetic cycle is exactly the reverse of the respiratory cycle in animals, in which oxygen is consumed and carbon dioxide excreted (see Carbon, and Air). Transpiration of water

by vegetation serves as an important means of maintaining atmospheric humidity.

Clothing and shelter for man come largely from the plant kingdom : cotton, linen, wood, and other cellulosic materials are obvious essentials in the maintenance of civilization.

Man has learned to adapt plant life to his requirements to a remarkable degree. Through selective breeding desirable plant characteristics have been enhanced, while undesirable ones have been suppressed or eliminated entirely. Through intelligent cultural practices, including the application of organic and inorganic supplements to deficient soils, it has been possible to increase crop yields to keep pace with rapid population increases. Better methods of controlling plant diseases and insect pests have also played an important part in increasing yields of desirable plants.

Without plant life, animal life could not exist. With further research, new and more productive plants will be produced the better to serve man and the animals on which he depends.

*References :* *The Chemical Investigation of Plants*, by L. Rosenthaler (G. Bell and Sons, London) ; *Plant Biology*, by Godwin (Cambridge University Press) ; *Plant Products*, by Collins and Reddington (Baillière, Tindall and Cox, London) ; *Baillière's Encyclopædia of Scientific Agriculture*, edited by H. Hunter (Baillière, Tindall and Cox, London) ; *Plant Biochemistry*, by James Bonner (Academic Press, New York) ; *Soil Conditions and Plant Growth*, by E. J. Russell (Longmans, Green and Co., London and New York) ; also Air, Bacteria, Cellulose, Chlorophyll, Fertilizers, Fibres, Nitrification, Plant Colouring Matters, Photocatalysis, Soils, and Vitamins.

**" PLASMOCHIN "** — See Pamaquin.

**" PLASTACELE "** (Du Pont) — Trade-mark for cellulose acetate thermoplastic resin. Possesses notable mechanical strength, impact resistance, machinability, and is self-extinguishing as to flames.

**PLASTER OF PARIS** — See Calcium (Sulphate).

**" PLASTEX "** — One of the " permitted explosives " which may be used in certain classes of mines.

**PLASTICITY** — See Plastometer.

**PLASTICIZERS (and Softeners)** are used in making lacquers in order to prevent brittleness in the films. They include triacetin, amyl tartrate, diethyl phthalate, dibutyl phthalate, diamyl phthalate, tricresyl phosphate, tributyl phosphate, butyl stearate, and castor oil, camphor and other substances. (See Lacquers, Pyroxylin, and Rubber.)

**PLASTICS** — The term actually includes all materials having plastic characteristics, such as rubber, moist clay, and heated glass, but is generally confined to organic materials that are either (1) thermoplastic, *i.e.*, plastic when heated, rigid upon cooling, plastic when reheated, such as celluloid, or (2) thermosetting, *i.e.*, setting upon

being subjected to heat and pressure, remaining rigid upon cooling, not softened when reheated, such as "Bakelite."

One of the oldest of these plastics is celluloid (see same), the basis of which is cellulose nitrated to about 11 per cent. nitrogen content. This has been made commercially since 1869, when J. W. Hyatt (Perkin medal award, 1914) and I. S. Hyatt, brothers, perfected the process. The phenol-formaldehyde resins were invented by Leo H. Baekeland (Perkin medal award, 1916; basic patents, about 1909) and named after him "Bakelite." In something like chronological order since then, some of the plastics—based on the substances named—that have appeared are: cellulose acetate (1911), casein (1919), glycerol-phthalic anhydride (alkyd; "Glyptal") (1927), urea-formaldehyde (1929), vinyl compounds ("Vinylite") such as chloride, alcohol, acetate, butyrate (1929), chloroprene ("Neoprene") (1930), alkene-polysulphide ("Thiokol") (1932), ethyl cellulose (1935), acrylates and methacrylates (1937), nylon (1938), styrene-butadiene (synthetic rubber) (1943), ethylene polymer (1943), silicones (1944), acrylonitrile ("Orlon") (1948).

The industry has grown rapidly to huge dimensions due in large part to the inherent properties, such as the ease of shaping and the desirable electrical behaviour, which place these materials in a class by themselves. Some idea of the magnitude and scope already attained by the industry may be comprehended by examining the report of production and uses (see Table).

TABLE SHOWING PRODUCTION AND USES OF SYNTHETIC RESINS,  
U.S.A., 1946

Production	Pounds	Uses	Pounds
Polyvinyl .. ..	156,000,000	Protective coatings	380,000,000
Phenol-formaldehyde	115,000,000	Moulding and casting	245,000,000
Glycerol-phthalic anhydride ..	111,000,000	Adhesives .. ..	78,000,000
Rosin esters .. ..	102,000,000	Treatment of paper, textiles, leather ..	46,000,000
Urea .. ..	77,000,000	Laminating .. ..	37,000,000
Styrene .. ..	73,000,000	Other uses, including glazing, sheeting, film, ion exchange	208,000,000
Melamine .. ..	14,000,000		
Other materials * ..	346,000,000		
Total Production	994,000,000	Total Uses .. ..	994,000,000

\* Other materials include such substances as cresols, xlenols, mannitol, sorbitol, ethylene glycol, pentaerythritol, methanol, resorcinol, cumarone, indene, furfural, fumaric acid, maleic anhydride, succinic acid, adipic acid, azelaic acid, acrylic acid, methacrylic acid, polyamides, aniline, silicones.

Thermosetting plastics require that the molecule has a double or triple bond, such as  $>C:C<$  (olefin),  $>C:O$  (carbonyl of aldehyde or ketone),  $-C:C-$  (acetylene), or  $-C:N$  (nitrile); more advantageously, a single carbon atom completely unsaturated, such as

$>C:C:C<$ ,  $>C:C:O$ , or  $>C:C:N-$ ; or still better a conjugated unsaturated carbon to carbon linkage, such as  $>C:\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}:C<$ ,  $O:\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}:O$ , or  $>C:\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}:N-$ .

Examination by X-ray shows repetition of unit structure throughout the resulting plastic or "high polymer." When this repetition is linear (fibre) the bonds are primarily chain-like or thread-like; when in two dimensions (film) the chain-like bonds are cross-linked to each other; and when in three dimensions (solid) the bonds are interlocked in length, width, and thickness.

A wealth of literature exists in this field, from which the following selections are presented, namely, "Synthetic Resins and Plastics," Symposium, *Ind. Eng. Chem.*, **28**, 1144-76 (1936); "Plastics as Engineering Materials," *Chem. and Met. Eng.*, September 1942, 100; *Modern Plastics Catalog* (Breskin Publishing Corp., New York); *British Plastics Yearbook* (Plastics Press, Ltd., London); *The Plastics Industry* (Modern Plastics Magazine, New York); *A.S.T.M. Standards of Plastics* (American Society for Testing Materials, Philadelphia); *Handbook of Plastics*, by Herbert R. Simonds, Archie J. Weith, and M. H. Bigelow (D. Van Nostrand Co., New York); *Plastics for Industrial Use*, by John Sasso (McGraw-Hill Book Co., New York); *Synthetic Resins and Allied Plastics*, by R. S. Morrell and others (Oxford University Press); "A Schematic Procedure for Identification of Commercial Plastics," by H. Nechamkin (*Ind. Eng. Chem., Anal. Ed.*, **15**, 40 (1943)); *Principles of High Polymer Theory and Practice*, A. X. Smith and C. A. Marlies (McGraw-Hill Book Co., New York); *Elastomers and Plastomers*, by R. Houwink, editor (Elsevier Publishing Co., New York and London); *Phenoplasts*, by T. S. Carswell (Interscience Publishers, New York); *The Chemistry and Technology of Plastics*, by Raymond Nauth (Reinhold Publishing Corp., New York); *The Chemistry of High Polymers*, by C. E. H. Bawn (Interscience Publishers, New York); *A Chemistry of Plastics and High Polymers*, by P. D. Ritchie (Interscience Publishers, New York); *The Chemistry of Commercial Plastics*, by R. L. Wakeman (Reinhold Publishing Corp., New York); *Rubbers, Plastics and Fibres*, by G. F. D'Alelio (John Wiley and Sons, New York); *Technical Data on Plastic Materials* (Plastics, Materials Manufacturers' Ass., Washington); see Plasticizers, and Gums and Resins (Synthetic).

**PLASTOMETER** — A variety of viscometer for the determination of viscosity and plasticity. (See *Fluidity and Plasticity*, by E. C.ingham (McGraw-Hill Book Co., New York); *Proceedings of the International Congress of Rheology*, 1948 (Interscience Publishers, New York); *Theoretical Rheology*, by Markus Reiner (Interscience Publishers, New York); and Viscosity.)

**PLATFORMING** — A catalytic reforming process using a platinum catalyst by Vladimir Haensel, in which cycloparaffin hydrocarbons are converted to aromatic hydrocarbons and paraffin hydrocarbons are

isomerized. This is accompanied by a marked lowering of the sulphur content of the resulting liquid hydrocarbons, and by an increase in octane rating by as much as 50 units (see *Ind. Eng. Chem.*, **42**, 585 (1950)).

**PLATINAMMINES** — Chemical compounds, many of which are of complicated structure, including tetrammine platinumous chloride ( $(\text{NH}_3)_4\text{PtCl}$ ). (See also Ammines, and Platinum Bases.)

**" PLATINITE "** — An alloy of nickel and iron (46 per cent. nickel) having approximately the same coefficient of expansion as glass, used instead of platinum for certain work in glassware—as, for example, electric incandescent lamps. It is frequently covered with a thin coating of copper, to which the glass adheres, and is then called " red platinum."

**" PLATINOID "** — The name of an alloy of German-silver character containing from 1 to 2 per cent. of tungsten.

**PLATINUM (Pt) and its Compounds** — Atomic weight, 195.23. See Elements for other data. Platinum is found naturally in the metallic state in small grains and nuggets in river sand and alluvial deposits in various regions, and especially the Ural Mountains; also as *iridosmine*, *sperrylite*, etc., in association with other rare metals, including palladium, rhodium, ruthenium, osmium, and iridium. Some nickel-copper-cobalt deposits at Shebandowan Lake, North Ontario, are rich in platinum. (See Sperrylite.) Up to 1914 Russia supplied over 90 per cent. of the world's output, estimated at under 300,000 ounces in 1913, 80,000 ounces in 1924, and later 100,000 ounces. A flotation process is used to remove the black sand accompanying the platinum in the concentrates. For details of Production and Import see *The Mineral Industry of the British Empire and Foreign Countries*, Imperial Institute, London, and *Minerals Yearbook*, U.S. Bureau of Mines, Washington.

Platinum is of a bright greyish-white colour, malleable and ductile, does not tarnish in the air, is heavier than gold, and of low electric conductivity. On account of its soft character it is usually alloyed with a small percentage of iridium to make articles of commercial service.

To obtain platinum from associated metals, the material is digested in *aqua regia* under some pressure, the solution evaporated to dryness, and the residue heated to 125° C. Any rhodium chloride is thus rendered insoluble, and upon extraction with water, acidification of the extract with hydrochloric acid, and addition of ammonium chloride, the red platinum ammonium chloride, ammonium chloroplatinate or ammonium platinichloride ( $(\text{NH}_4)_2\text{PtCl}_6$ ) is produced and crystallized out (the corresponding iridium salt, so far as it is present, being left in the mother-liquor), and from the salt spongy platinum is obtained upon ignition, and may be hammered into a concrete mass or melted in the oxyhydrogen flame.

" Spongy platinum " is obtained by igniting the ammonium chloroplatinate above described; while " platinum black " is a soft black powder which results from the precipitation of platinum solutions by

means of reducing agents. In both of these forms the metal exhibits the property of condensing gases on its surface in a high degree, and a mere fragment of the spongy metal, when introduced into a mixture of hydrogen and oxygen gases in the proper proportions, at once causes an explosion with formation of water. Even when cold, platinum has the property of condensing oxygen on its surface. In the forms described, and in that of gauze, the metal is used as a catalyst, for example, as platinum black deposited on anhydrous magnesium sulphate for the reaction  $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$ , and as smooth platinum (gauze) in the oxidation of ammonia to nitrogen oxides and nitric acid. This catalytic action is easily interfered with by traces of many substances, phosphine being one of such "poisons," as they are termed.

### PLATINUM AND ALLIED METALS, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

					Troy Ounces (1 ounce equals 480 grains or 31.1 grams)
Country					
U.S.S.R.	..	..	..	..	100,000*
Canada	..	..	..	..	270,000
U.S.A.	..	..	..	..	37,000
					<hr/>
Colombia	..	..	..	..	307,000
					34,000
Union of South Africa	..	..			56,000
					<hr/>
Sum of above	..	..	..	..	497,000
WORLD PRODUCTION	..	..	..	..	519,000

\* Estimated.

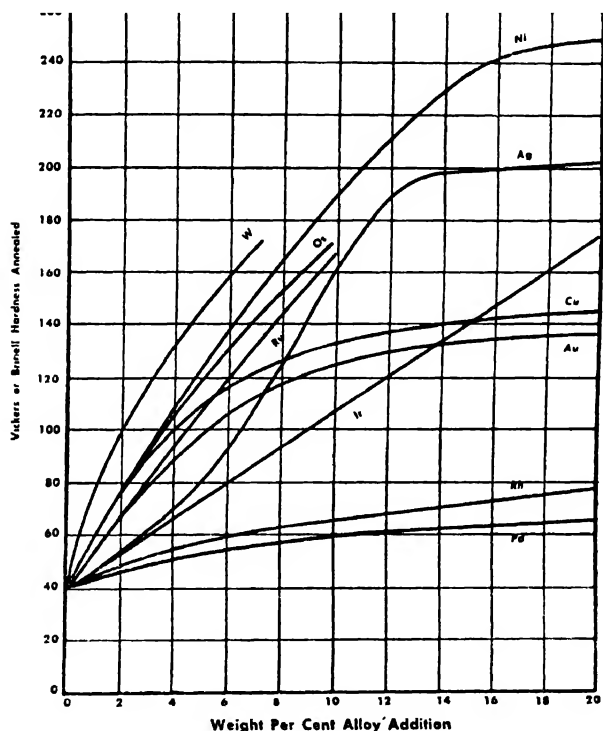
Platinum forms alloys with many metals, and the introduction of 10 per cent. iridium produces a combination which is even more resistant to chemical action than the pure metal.

The jewellery trade is the predominant factor in the platinum market, while in chemical industry it is used for making stills for the concentration of sulphuric acid, also in the electro-chemical industry, while its uses as a catalyst have already been referred to. An alloy used by jewellers consists of 1 part platinum, 1 part copper, and 2 to 5 parts silver. "Platinor" consists of 2 parts platinum, 5 parts copper, 1 part silver, and 1 part nickel. One form of so-called "mock-gold" consists of 7 parts platinum and 16 parts copper. Platinum bronze is made of 1 part platinum, 90 parts nickel, and 9 parts tin; whilst a variety of dentists' alloy is made of 5 parts platinum, 3 parts gold, and 4 parts palladium.

In the forms of crucibles, dishes, foil, spatulas, weights, wire, etc., platinum is largely used in laboratories on account of its capability of withstanding exposure to a high degree of heat and its being unattacked by many chemicals—although it is attacked at a red heat

by alkalis, nitrates, cyanides, phosphorus, arsenic, and similar substances. Care has to be taken that it is not exposed to the action of other molten metals such as lead, as the two metals will form an alloy if exposed to a sufficiently high temperature, and result in the ruin of the platinum, which is a very costly metal.

In the form of foil, as held by a pair of tongs in the hands, it is useful for testing the action of heat upon chemical substances placed on



Graph Showing Hardening Effect of Alloying Additions on Platinum

Courtesy of The American Platinum Works, Newark, New Jersey, U.S.A.

its surface, the foil being placed directly over the flame of a spirit-lamp or Bunsen burner. It can thus be ascertained whether they fuse or char (indicating the presence of organic matter), or are volatile, or give off a distinctive smoke or odour; and if they burn, whether they do so with any notable feature or communicate any particular colour to the flame to which they may be exposed, etc.

Platinum can be dissolved by nitrohydrochloric acid (*aqua regia*).

**Platinum Crucibles** are most useful for exposing substances to heat with the view of burning off volatile or organic constituents, or of fusing refractory substances with added chemicals (fluxes) in order to obtain them in a form soluble in some menstruum.

**Platinum Dishes** are utilized for evaporation of solutions which are likely to attack glass or porcelain.

**Platinum Weights** of small size are valuable because the metal does not tarnish in the air, and the weights are not easily corroded by accidental contact with chemicals as are copper and brass weights; 0.5 gram and smaller ones are among those frequently employed.

**Platinum Wire** is useful for stirring liquids which attack glass rods, and for exposing liquids or solids spread over its surface to the flame of a Bunsen burner, in order to tone the distinctive features attendant thereon. For this application the wire is bent into a loop at one end, so that a bead of the liquid or solid to be tested may be held thereon, the other end of the wire being held by tongs, or fixed in a wooden handle, or fused into a glass tube. (See Boron (Borax).)

**Platinum (Colloidal)** can be made by disintegration of the metal by spluttering platinum electrodes under water, or by heating the metal to red heat and plunging it into water, or by grinding the metal. It can also be made by reducing platinum compounds with reducing agents, such as (a) magnesium and hydrochloric acid; (b) formaldehyde; (c) most aldehydes, except benzaldehyde; (d) hydroxylamine; and (e) many other reducing reagents. The stability of the colloid can be increased by using protective "gel" colloids.

When hydrogen gas is passed into a reddish-brown colloidal solution of platinum the latter becomes dark brown, and hydrogen is adsorbed. This colloidal platinum solution catalyses many hydrogen reductions such as, acetylene to ethylene and ethane, the hydrogenation of unsaturated oils, and the reduction of ferric salts to ferrous salts. Colloidal platinum also catalyses the oxidation of carbon monoxide to carbon dioxide, hydrogen to water, and many other reactions. It also catalyses the decomposition of hydrogen peroxide to oxygen and water. The catalytic activity of colloidal platinum is increased by ultra-violet light, but too long exposure will cause precipitation. The catalytic activity of colloidal platinum is poisoned by sulphides and cyanides.

There are three **oxides**, namely, platonic oxide ( $\text{PtO}_2$ ), platino-platinic oxide ( $\text{Pt}_3\text{O}_4$ ), and platinous oxide ( $\text{PtO}$ ), all of which are black and insoluble in water; and two **hydroxides**, namely, platonic hydroxide ( $\text{Pt}(\text{OH})_4$ ), and platinous hydroxide ( $\text{Pt}(\text{OH})_2$ ).

There are two **chlorides**, namely, platonic chloride ( $\text{PtCl}_4$ ), obtained by dissolving platinum in aqua regia, and it is a yellowish-red crystalline salt soluble in water and alcohol; and platinous chloride ( $\text{PtCl}_2$ ), a green powder and insoluble in water, used to some extent in the platinotype photographic process. It forms double salts with some other chlorides, for example, potassium chloroplatinite ( $\text{K}_2\text{PtCl}_4$ ) (a red salt soluble in water and used in photography), and the ammonium chloroplatinite ( $(\text{NH}_4)_2\text{PtCl}_4$ ). Platonic chloride similarly forms double salts: potassium chloroplatinate ( $\text{K}_2\text{PtCl}_6$ ), a yellow crystalline body only slightly soluble in cold water, and decomposed upon heating into potassium chloride, chlorine, and free platinum; the ammonium compound ( $(\text{NH}_4)_2\text{PtCl}_6$ ), less soluble than the potassium

salt in cold water, and, when similarly heated, reduced to pure platinum; and the sodium salt ( $\text{Na}_2\text{PtCl}_6$ ), which is reddish-yellow and readily soluble in water. Chloroplatinic acid ( $\text{H}_2\text{PtCl}_6 \cdot \text{H}_2\text{O}$ ), prepared by the action of aqua regia on the metal, followed by evaporation of the solution and crystallization, is a red-brown crystalline substance, soluble in water and alcohol, used in electroplating, preparing platinized catalysts, and making indelible ink.

Two **sulphides**, namely, platonic sulphide ( $\text{PtS}_2$ ), and platinous sulphide ( $\text{PtS}$ ), are known, both of which are black and insoluble in water.

The **cyanide** ( $\text{Pt}(\text{CN})_2$ ) combines with other cyanides to form double salts, known as platinocyanides, for example, potassium platinocyanide ( $\text{K}_2\text{Pt}(\text{CN})_4$ ).

There is a series of **platinammonio** compounds similar to the cobalt-ammines (see Ammines), one group being derived from the chloride  $\text{PtCl}_4$  and another from  $\text{PtCl}_2$ . These compounds are regarded as containing certain molecules of ammonia co-ordinated with the metal. In the platinous series there are two isomeric compounds ( $\text{NH}_3$ )<sub>2</sub> $\text{PtCl}_2$  (cis- and trans-) and a polymeride (( $\text{NH}_3$ )<sub>4</sub> $\text{Pt}$ ) $\text{PtCl}_4$  known as the *green salt of Magnus*. There are many ammines of the platonic series. The pentammine ( $\text{PtCl}_5\text{NH}_3$ ) $\text{Cl}_3$  and hexammine are produced by the action of liquid ammonia on ammonium chloroplatinate.

**PLATINUM BASES (Organic)** — Combinations of salts of the amines, such as the chlorides, with platonic chloride, for example, methylamine chloroplatinate (( $\text{CH}_3\text{NH}_3$ )<sub>2</sub> $\text{PtCl}_6$ ). (See Ammines, and Platinum Compounds.)

**PLESSY'S GREEN** — See Chromium (Phosphate).

“**PLOMBIT**” — An acid-resisting material of m.p. 130° C., said to be a combination of hard rubber and oleic acid with concentrated sulphuric acid and sulphur.

**PLUMBAGO** — Another name for graphite or black-lead. (See Carbon.)

**PLUMBATES** — See Lead (Dioxide).

**PLUTONIUM** (Pu) — Element number 94, probable atomic weight 239, discovered by G. T. Seaborg, E. M. McMillan, J. W. Kennedy, and A. C. Wahl, in 1940, and accepted (1949) by the International Union of Chemistry. Plutonium was made by bombardment of uranium by deuterons, which resulted in an isotope of neptunium, and this isotope decayed to plutonium 238; neptunium 239 decays by beta-particle emission to form plutonium 239. Plutonium 239 undergoes fission with slow neutrons. In September, 1942, B. B. Cunningham and L. B. Werner, of the Metallurgical Laboratory, University of Chicago, isolated a few micrograms of plutonium 239, thus signaling the first success of man in producing a visible amount of a synthetic element. The element is made in quantity at Hanford, Washington State, U.S.A. (See Nuclear Chemistry.)

**PNEUMATIC TROUGH** — An apparatus for the collection of gases over water (so far as they are insoluble in that medium), while in some other cases mercury is employed. In the former case it consists of a vessel

## 864 PNEUMATIC TROUGH — POISONS AND ANTIDOTES

of glass or metal provided with a shelf situated at one end at a depth of 2 or 3 inches from the top. The vessel for collecting the gas is filled with liquid and placed mouth downwards over a funnelled hole provided in the shelf, underneath which the delivery tube conveying the gas from the generator is placed, the bubbles of gas passing up and displacing the liquid contents of the collecting vessel. When mercury is employed, the trough is usually made of stoneware, glass, or porcelain.

**PODOPHYLLIN** — See Gums and Resins.

**POISE** — See Centipoise.

**POISON GASES** — See Gassing.

**POISONS AND ANTIDOTES** — Among other antidotes against poisons may be noted :

Acids .. ..	Magnesia, lime, or chalk made into a milk with water.
Aconite .. ..	Stomach-pump or emetic.
Alkalis .. ..	Emetic, followed by dilute vinegar.
Antimony .. ..	Emetic, decoction of bark or strong tea, and keep warm.
Arsenic .. ..	Emetic, followed by freshly precipitated ferrous oxide, or white-of-egg beaten up in milk, or magnesia.
Benzene .. ..	Emetic, fresh air, and artificial respiration when necessary.
Petroleum .. ..	
Paraffin .. ..	
Chlorine .. ..	Magnesia. (See also Gassing.)
Chloral .. ..	Emetic, keep awake, and artificial respiration when necessary.
Chloroform .. ..	
Carbolic acid .. ..	Olive oil, emetic or stomach-pump, followed by stimulants.
Carbon disulphide	Stomach-pump, warmth, stimulants, and artificial respiration.
Carbon monoxide ..	Inhalation of oxygen and artificial respiration.
Carbon tetrachloride	Strong tea or coffee, and such cardiac stimulants as used in chloroform poisoning.
Copper .. ..	Encourage vomiting, then give eggs beaten up in milk.
Corrosive sublimate }	
Lead salts .. ..	Sodium sulphate or magnesia.
Laudanum .. ..	Emetic or stomach-pump, or purified charcoal powder if swallowed immediately after the poisoning, and keep patient well awake.
Morphia .. ..	
Opium .. ..	
Nitrous gas .. ..	Early use of ammonia.
Oxalic acid .. ..	Chalk and water freely.

One of the best **emetics** is mustard, using half a tablespoonful mixed in half a tumbler of water, and for children one or two teaspoonfuls of

ipecacuanha wine every ten minutes. Another good emetic for adults is a teaspoonful of sulphate of aluminum (alum).

Lead dust present to a less extent than 5 milligrams per 10 cubic metres is alleged to be comparatively innocuous, and 2 milligrams is the daily dose that a worker can absorb and escape chronic poisoning.

It has been found that 20 parts of benzol per 10,000 parts air is on the border-line of poisoning.

Among the poisons responsible for fatalities are corrosive sublimate, coal gas, sulphuric acid, arsenic, nitric acid, ammonia, vermin-killers, chloral hydrate, belladonna, aconitine, hyoscyne, phosphine, and tartar emetic. (See A. Wynter Blyth and M. Wynter Blyth on *Poisons* (Charles Griffin and Co., London); *A Practical Handbook on Rat Destruction*, by C. L. Claremont (John Hart, London); *Industrial Toxicology*, by Alice Hamilton (Harpers, New York); *Toxicity of Industrial Organic Solvents* (H.M. Stationery Office, London); *Poisons. Their Chemical Identification and Emergency Treatments*, by Vincent J. Brookes and Hubert N. Alyea (D. Van Nostrand Co., New York.)

For further information concerning chemical poisoning and industrial diseases, readers are referred to the Annual Reports of the Chief Inspector of Factories and Workshops. (See also Bacteria, Food Poisoning, Gassing, Hazardous Chemicals, and Insecticides.)

**POLARISCOPE (Polarimeter)** — See Polarization.

**POLARIZATION** — A Nicol prism (analyser) composed of Iceland spar—pure crystallized calcium carbonate—split along a diagonal plane and then cemented together again with Canada balsam, gives a pencil of light the vibrations of which are in one plane only, and light so obtained is said to be polarized. Many liquids exhibit optical activity and effect the rotation of a ray of polarized light when placed in a column between two Nicol prisms in a suitable instrument. Polarimeters (polariscopes) are the various instruments used to measure the angle through which the polarized ray is turned to the right or to the left. Substances which rotate the ray of polarized light to the right are termed dextro-rotatory, and those which rotate it to the left are termed lævo-rotatory. (See Invertase, and Tourmaline.)

**POLAROGRAPHY** — This is a special technique for the study of chemical phenomena that take place at the cathode of an electrolytic cell. By means of the technique both qualitative and quantitative aspects can be studied of oxidizing or reducing solutions. Polarography is based on the observation that each solute, whether ion or molecule, requires its own particular potential to be attained before it undergoes chemical change. The polarograph, which enables this potential to be observed, consists of an apparatus having in the electrical circuit a dropping mercury cathode, an electrolyte, and a plain mercury anode, and also allows the potential to be gradually changed and the corresponding values of the current passing through the cell to be determined. The discharge of an ion or the occurrence of a new process at the cathode is indicated by a sudden increase in the current with only a small increase of potential. The concentration of the solute (electrolyte) is directly

proportional to the amount of current at the moment when the new reaction appears.

*References:* *Polarography*, by I. M. Kolthoff and J. J. Lingane (Interscience Publishers, New York).

“**POLAWAX**” — See Waxes.

**POLENSKI VALUE** — See Fats (Tests).

**POLLUX (Pollucite)** — A complex silicate containing cesium, occurring in *pegmatite*, found in Maine, etc.; crystal system No. 1, and sp. gr. 2.86.

**POLONIUM (Po) (Radium F)** — A radioactive element, obtained from pitchblende; is a degradation product of radium; forms a sulphide analogous to that of bismuth. Atomic number 84, and all its isotopes are radioactive, the longest-lived natural isotope being polonium 210, but J. J. Howland, D. H. Templeton, and I. Perlman report artificial polonium 208 of still longer life (*Phys. Rev.*, **71**, no. 8, 552 (1947)). Discovered by Mme Curie, in 1898. (See Nuclear Chemistry, and Radioactivity.)

**POLYBASITE** — A mineral sulphide of silver and antimony (other metals being associated), found in some parts of the United States and elsewhere (crystal system No. 4, and sp. gr. 6.2).

**POLYMERIZATION** — A reaction between like chemical units forming multiple-weight compounds, such as paraformaldehyde  $((\text{HCHO})_x)$ , a solid by evaporation of formaldehyde solution; trioxymethylene  $((\text{HCHO})_3)$ , a solid from liquid formaldehyde; paraldehyde  $((\text{CH}_3\text{CHO})_3)$ , a liquid of b.p.  $124^\circ\text{C}$ . by treatment of acetaldehyde with concentrated sulphuric acid; metaldehyde  $((\text{CH}_3\text{CHO})_4)$ , a solid by treatment of acetaldehyde with acid at low temperature.

Hydrocarbons of low molecular weight are polymerized to hydrocarbons of high molecular weight by the aid of a catalyst, such as phosphoric acid. V. N. Ipatieff and B. B. Corson (*Ind. Eng. Chem.*, **28**, 860 (1936)) report a yield of 4.7 gallons (U.S.) of 82 octane number gasoline per thousand cubic feet of ethylene by the use of a gauge pressure of 520 pounds per square inch and a temperature of about  $600^\circ\text{F}$ . G. Egloff (*Ind. Eng. Chem.*, **28**, 1461 (1936)) states that the catalytic polymerization process operates upon olefin-containing gases at  $450^\circ\text{F}$ . and 200 pounds per square inch pressure to produce a liquid boiling in the gasoline range. (See Petroleum (Cracking).)

Polymerization is the process responsible for the formation of plastics (see same, and Polymerism).

**POLYMERISM** — The phenomenon exhibited by a substance, two or more molecules of which combine to form a compound of the same percentage composition but having a molecular weight differing from that of the monomer by a multiple of two or more. During the condensation nothing is eliminated, and the resulting substance is called a polymer of the original substance. Acetaldehyde, for example, under the influence of a drop of concentrated sulphuric acid, rapidly polymerizes to the trimer, paraldehyde  $(\text{C}_2\text{H}_4\text{O})_3$ , differing in certain

properties from the simple aldehyde, but rapidly reconverted to it by distilling with dilute sulphuric acid. This is an example of reversible polymerization, but in many cases the product cannot be readily reconverted to the starting material, for instance, the sugar-like polymers of formaldehyde, and some artificial resins, such as polystyrene and polyethylene.

**POLYMIXIN** — An antibiotic substance, isolated from the culture filtrates of *Bacillus polymixa*, possessing a high bactericidal activity against certain Gram-negative bacteria but relatively no activity against Gram-positive organisms. It has been shown to have a beneficial effect against experimental infections in mice due to *Klebsiella pneumoniae*, *Pasteurella multocida*, and fowl typhoid (see P. G. Stansly and M. E. Schlosser, *J. Bact.*, **54**, 549 (1947)). It is closely related to bacillosporin (see same).

**POLYMORPHISM** — The existence of an element or compound in two or more crystalline forms, for example, rhombic sulphur and monoclinic sulphur, and calcite and aragonite forms of calcium carbonate.

**POLYPEPTIDES** — Hydrolysed derivatives of proteins resembling peptones in some respects, in which two or more so-called amino-acid groups are combined—the carboxyl group of one acid condensed with the amino group of another. (See *Advances in Protein Chemistry*, Vol. I (Academic Press, New York); Albumins, Enzymes, and Proteins.)

**POLYSACCHARIDES** — See Carbohydrates.

**POLYTHENE** (Du Pont) — Generic name for synthetic plastic based on polymerized ethylene, having excellent electrical insulating property and used for this purpose in electronic apparatus. Possesses notable resistance to water and water vapour, toughness at low temperatures, and resistance to chemicals.

**PONTIANIC RESIN** — See Gums and Resins.

**POPPY SEED OIL** is expressed from the seeds of the black or opium poppy (*Papaver somniferum*, var. *nigrum*), which yield about 36 to 40 per cent. It is odourless, soluble in ether, chloroform, and carbon disulphide, solidifies at  $-18^{\circ}\text{C}$ ., and is one of the drying class of oils. It resembles olive oil in appearance, and contains about 8 per cent. of solid fatty acids, 30 per cent. oleic acid, 60 per cent. linoleic acid, and 5 per cent. linolenic acid. Its sp. gr. is 0.925, sap. v. 193 to 195, i.v. 133 to 143, and ref. ind. 1.457 at  $60^{\circ}\text{C}$ . It is used as food in some parts of Germany and France, and for mixing with light colours for use in painting, after being bleached in the sun; also in soap-making, for adulterating olive oil, and in varnish-making. (See Argemone Oil.)

**POPULIN (or Benzoyl Salicin)** ( $\text{C}_{20}\text{H}_{22}\text{O}_8$ ) — A soluble glucoside contained in the bark, leaves, and root of the aspen (*Populus tremula*), and which can be artificially made from benzoyl chloride ( $\text{C}_6\text{H}_5\text{COCl}$ ), and salicin ( $\text{C}_{18}\text{H}_{18}\text{O}_7$ ). It yields salicin and benzoic acid upon hydrolysis.

**PORCELAIN AND EARTHENWARE** articles are made largely of clay coated or glazed with some substance that fuses at a high temperature,

thus giving them a coating and at the same time binding the body of the material together in coherent mass. The normal (triaxial) porcelain mixture may be said to consist of 50 per cent. clay, 25 per cent. quartz, and 25 per cent. felspar. The best quality of china clay or kaolin (aluminium silicate) is used for porcelain goods (which are fired at the highest temperature and are vitreous in structure) and the poorer qualities of clay for earthenware articles, the glaze for the former being felspar alone or mixed with quartz and lime in finely powdered form suspended in water, into which mixture they are dipped or coated by brushing before firing. In making "spode china" bone phosphate is used, and gives the best quality of porcelain in respect of durability. Earthenware bodies contain as a rule about 70 per cent. total silica, the materials used being ball clay, china clay, and flint. A published analysis of a superior English product shows a content of 66.17 per cent. silica, 29.40 per cent. alumina, and small proportions of ferric oxide, phosphoric acid, lime, magnesia, soda, and potash.

"Cornish stone" (derived from *pegmatite*) consists of approximately equal parts of felspar, quartz, and clay, and is therefore a ready-made material. The high-fire glazes vary in composition according to the articles to be treated, those for chemical porcelain consisting of varying proportions of silica and alumina, together with certain proportions of lime and potash. For earthenware goods, a "salt glaze" is used and applied by introducing salt into the furnace containing the ware, in which it is volatilized and decomposed by the heated surfaces of the articles, causing the formation of a fusible double silicate of sodium and aluminium on their surfaces.

Small articles are built up on the potter's wheel, but larger ones are more readily made by building up with plastic clay or by the use of "slip" (a mobile suspension of clay in water made by deflocculating clay with alkali or sodium silicate), followed by casting in plaster moulds, or by the use of machine moulds.

Articles of stoneware, such as jars and drain-pipes, are fired at a high heat and salt glazed, while for many varieties of earthenware, which are fired at a comparatively low heat, easily fused glazes containing lead or borax are used. The use of lead compounds is viewed with growing disfavour by reason of their poisonous effects in pottery works. Lead silicate containing about 65 per cent. lead oxide combined with 35 per cent. silica is now being used largely as a glaze in pottery work, having a solubility of less than 5 per cent. when determined by the Thorpe solubility test under the Lead Regulations. For fine qualities of ware, such as Delft and Majolica, the surfaces are coated with opaque white glaze containing stannic oxide ( $\text{SnO}_2$ ).

The white-glazed sanitary fire-clay goods are a refined class of stoneware made from clays of very similar colour and character, but more refractory to heat at a kiln temperature of about  $1,250^\circ \text{C}$ . The colour is obtained by introducing an intermediate layer of white substance between the clay and the finishing glaze, muffle kilns being used to maintain an oxidizing atmosphere and to exclude dust.

The clays used in making porcelain and earthenware lose their chemi-

cally associated water when heated to from  $480^{\circ}$  to  $600^{\circ}$  C., an operation that must not be carried out with too great speed due to the danger of thereby distorting the shape of the objects. The temperature used in making non-absorbent or vitreous porcelain ranges from  $1,250^{\circ}$  to  $1,550^{\circ}$  C., and that for porous or non-vitreous ware from  $1,150^{\circ}$  to  $1,250^{\circ}$  C. Hard porcelain melts at about  $1,680^{\circ}$  C., although it becomes soft below that temperature, so that unglazed porcelain can be used only up to  $1,400^{\circ}$  C. and the glazed quality up to  $1,200^{\circ}$  C. (see Refractories).

Chemical stoneware consists of a mass of refractory matter held together or cemented by vitrifying selected clays. On the one hand, coarse-grained chamotte bodies of fire-brick nature are used, as, for example, for conveying acid gases at high temperature; and, on the other hand, fine-grained porcelain bodies, as required for large storage-battery tanks used for electrical purposes, with an infinite number of varieties in between these two extremes, so that as no one clay meets all these requirements, it is often necessary to make mixtures of several kinds to obtain the desired qualities.

One published typical analysis of chemical stoneware is given as follows, and this resists all acids excepting such as act on silica, for example, hydrofluoric acid:

SiO <sub>2</sub>	..	..	..	..	..	..	73.23	per cent.
Al <sub>2</sub> O <sub>3</sub>	..	..	..	..	..	..	22.27	"
Fe <sub>2</sub> O <sub>3</sub>	..	..	..	..	..	..	0.58	"
CaO	..	..	..	..	..	..	0.58	"
K <sub>2</sub> O	..	..	..	..	..	..	2.02	"
Na <sub>2</sub> O	..	..	..	..	..	..	1.42	"
Loss on ignition	..	..	..	..	..	..	0.06	"

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100.16

Some qualities of ware, such as flower-pots, etc., are not glazed, and this is true also of Spanish cooling vessels (alcarazzas), which are specially made porous in order to maintain a constant, slow evaporation and consequent cooling of the water contained in them (see Porosity).

Fracture in porcelain is not supposed to be wholly the result of crystallization, but that of attempted crystallization under stress—that is to say, to the possibility or otherwise of the adaptation of the matrix of the porcelain body of the crystals which develop in the heart of it. Steatite, china clay, kaolin, and felspar are used in the manufacture of highly efficient insulating products for the electrical industry. The behaviour of various feldspars in vitreous bodies has been studied by Geller and Creamer, who show that the refractoriness increases and the softening range decreases with increase of K<sub>2</sub>O. (See *Ceramic Industry*, by H. H. Stephenson (Davis Bros., London); *Ceramics, Clays, Refractories, Saggars, Shales*, "Sillax," Sillimanite, and Steatite.)

**POROSITY** — The ratio of the volume of the pores or voids, between the solid particles in a refractory body or brick, to the volume of the whole body, usually expressed in per cent., is called porosity. Generally the volume of the pores is determined by the amount of water absorbed

by the body. Since the water does not penetrate the closed or sealed pores the result obtained is a measure of the apparent porosity or a measure of the open pores.

Porosity is a phenomenon that affects many materials, but is most commonly met in the field of ceramics. The following table indicates the porosity of some common refractories :

Type	Average Porosity Per Cent.					
Fire-clay .. .. .	..	..	..	..	..	20-40
Kaolin .. .. .	..	..	..	..	..	18
Alumina .. .. .	..	..	..	..	..	32
Magnesite .. .. .	..	..	..	..	..	23
Silica .. .. .	..	..	..	..	..	25
Silicon carbide, clay bonded .. .. .	..	..	..	..	..	20
Fire brick .. .. .	..	..	..	..	..	75-90

The permeability or porosity of a porous body is that property which permits a gas or other fluid to flow through it. It is measured by the rate of flow of a standard fluid under a definite pressure. The permeability of a body depends upon the number, size, and shape of the interconnecting pores. Pores which are sealed have no effect upon permeability.

The porosity of a refractory is of great importance, as a low porosity, in general, gives better resistance to spalling (a condition of breaking or cracking in service to an extent where pieces separate and fall away leaving new surfaces exposed) and has high thermal conductivity; whereas high porosity gives high insulating value, and good permeability.

Porosity is controlled in ceramic materials by moulding conditions, where high pressure gives a dense structure; by firing temperature, where high-temperature firing gives low porosity; and by controlling the grog size. Pores are produced by introducing into plastic ceramic mix (a) an organic material such as peat, straw, sawdust, or cork that can be burned out to leave voids; (b) a material such as flake naphthalene that can be sublimed out; (c) stable air bubbles formed in the mix by limestone and an acid, or by zinc and an alkali or by using a preformed foam.

The permeability of refractories is utilized to allow the flow of gases in recirculating type furnaces, in thermocouples, in muffles, and in recuperators; also in diffusion work involving the separation of gaseous constituents based upon Graham's law of diffusion, which states that the rate of diffusion is inversely proportional to the square root of the density of the gas. This principle is one of the methods utilized in separating gaseous compounds of uranium 235 from uranium 238 by using long lines of porous diffusion plates. Porous diffusion bodies are produced from carbon, graphite, alundum, and silicon carbide to perform such tasks as filtering solutions, and for dispersing gases for absorption in sewage treatment.

*Reference: Refractories*, by Norton (McGraw-Hill Book Co., New York).

**PORPHIN** — The simplest unsubstituted porphyrin, consisting of four pyrrole nuclei joined in the alpha positions through CH- groups to form a flat, sixteen-membered ring. It was synthesized by Hans Fischer in 1935, and its derivatives form the skeletons of hæmoglobin and chlorophyll.

**PORPHYRITES** — Crystalline igneous rocks.

**PORPHYRY** — A form of felspar or felspathic base.

**PORPOISE OIL** — See Fish Oils.

**PORTLAND CEMENT** — See Cement.

**PORTLAND STONE** — A granular oölitic limestone (calcium carbonate) found near Portland, England, and this is the derivation of the term Portland cement, in that the latter resembled the Portland building stone.

**POSITRON** — The positively charged electron, discovered by C. D. Anderson in 1932 by means of their ionization tracks in air of a Wilson cloud chamber, and later found to be emitted when gamma rays of very high frequency from a radioactive element are intercepted by a plate of metal. Certain radioactive nuclei emit positrons just as others emit electrons. Mass of positron,  $1/1800$  that of the mass of the hydrogen atom; and charge of positron, unit positive charge. (See Nuclear Chemistry.)

**POTASH** — See Potassium (Compounds).

**POTASH ALUM** — See Aluminium (Alums).

**POTASH BULBS** — See Organic Analyses.

**POTASSIUM (K) and its Compounds** — Atomic weight, 39.096. See Elements for other data. Potassium occurs abundantly in nature at Stassfurt, Germany, in the form of saline deposits of various compositions, as chloride (KCl) in *sylvinite* (*sylvine*), as a double chloride of potassium and magnesium ( $KCl, MgCl_2, 6H_2O$ ) in *carnallite*, and as a compound sulphate and chloride ( $K_2SO_4, MgSO_4, MgCl_2, 6H_2O$ ) in *kainite*, the most popular potash manure. There are somewhat similar and even richer deposits in Alsace, in the early strata of the Tertiary period (mostly pure sylvinite, carnallite being absent), estimated as sufficient for furnishing more than 300,000,000 tons calculated as potassium oxide ( $K_2O$ ). There are also large deposits at Catalonia, Kalusz (in the Carpathian region of Galician Poland), at Solikamsk in Russia, while in the Italian colony of Eritrea considerable deposits were found and worked during World War I. The Alsatian sylvinite is a mineral mixture of potassium and sodium chlorides with some 9 to 14 per cent. insoluble matter (chiefly white clay and iron oxide), 0.5 to 1.2 per cent. water, 2 to 5 per cent. calcium sulphate, and a small proportion of magnesium chloride. After grinding, it is used as produced, or refined to a content of some 80 per cent. KCl.

Extensive deposits of potash have been discovered and are being

worked in New Mexico (U.S.A.), and the brine of Searles Lake, California (U.S.A.) is also used for potash. Very extensive investigations were conducted in the United States during World War I, and the results are well displayed in several volumes of *Mineral Resources of the United States* (U.S. Geological Survey, Washington, D.C.) at that time and subsequently.

It is estimated that the saline water of the Dead Sea contains, among other ingredients, 2,000 million metric tons of potassium chloride.

Nitrate and chloride of potassium are also found in association with sodium nitrate in the nitrate deposits of Chile and Peru, and in some of the Chinese provinces, while the *greensands*, of which large deposits are found along the Atlantic seaboard of the United States, contain some 6 to 7 per cent. of potash said to be recoverable by digestion with slaked lime at 200° C.

Potassium compounds are found in the soil as products of decomposition of certain rocks (for instance, feldspar), from which they find their way into vegetable life, and so into the bodies of the animals that feed upon it, thus accounting for their presence in the *suint* or fat that is extracted from sheep's wool.

Potassium compounds can be recovered to some extent from the flue gases and dust of iron blast-furnaces and Portland cement kilns. Blast-furnace gas contains from 4 to 6 grams solid particles per cubic metre, yielding about 27 per cent. of potassium chloride in the recovered particles. Common salt is introduced with the blast charge, and this, in reaction with the potassium contained in the iron ores, forms potassium chloride, which volatilizes and can be recovered from the fume and dust. It has been proposed to use potassium-bearing minerals, such as *feldspar*, as a part of the charge in cement kilns for the express purpose of recovering the potash by volatilization.

There is also a process for recovering potash ( $K_2CO_3$ ) from molasses.

Potassium chloride is now chiefly obtained from *carrollite* and to some extent from *leucite* ( $K_2O, Al_2O_3, 4SiO_2$ ) (which in the pure state contains 21.5 per cent.  $K_2O$ , 23.5 per cent.  $Al_2O_3$ , and 55 per cent.  $SiO_2$ , and is a constituent of the volcanic lavas which abound in Italy) by treatment with hydrochloric acid and further appropriate operations. By another process potash alum is obtained, using sulphuric acid for dissolving the potassium and aluminium constituents of the crushed material. (See Leucite.)

*Alunite* (see same) is another mineral which is a potential source of potassium compounds. Kelp (see same) is a possible source of potash ( $K_2CO_3$ ) by burning to ash.

The metal potassium is silver-white, lustrous, soft and rapidly oxidizes in the air, its vapour taking fire, so that in the metallic state it has to be preserved in naphtha or kerosene.

It was formerly obtained by heating a mixture of potassium carbonate and carbon, the metal thus liberated distilling over and being collected in naphtha, but it was a difficult process and has been superseded by another in which fused potassium hydroxide or chloride is subjected to electrolysis, potassium being set free at the cathode, where it floats to

the surface of the fused mass and is withdrawn from time to time under special precautions.

*Reference:* *Potash*, by J. W. Turrentine (John Wiley and Sons, New York).

When potassium salts in aqueous solutions are electrolysed, the metal set free reacts at once with the water and forms potassium hydroxide in solution, but if the concentration of the salt be increased to saturation the metal may be collected by solution in mercury when the latter is used as cathode.

In common with sodium, potassium decomposes water, hydrogen being liberated.

See Symposium on Potash in *Ind. Eng. Chem.*, **30**, 853–896 (1938).

#### POTASH MINERALS, WORLD PRODUCTION

Annual average for the three-year period 1937–1939

Data arranged and rounded off by the Editor.

Country				Potash Minerals as $K_2O$ Content Metric Tons
Germany	..	..	..	2,070,000
France	..	..	..	560,000
Poland	..	..	..	100,000
Spain	..	..	..	30,000*
				<hr/>
U.S.S.R.	..	..	..	2,760,000
				200,000*
U.S.A.	..	..	..	280,000
Palestine	..	..	..	30,000
				<hr/>
Sum of above	..	..		3,270,000

WORLD PRODUCTION, approximately the above.

\* Estimated.

**Oxides** — Potassium oxide ( $K_2O$ ) can be obtained by the oxidation of potassium, as a grey crystalline body of sp. gr. 2.32, and when dissolved in water it forms a solution of potassium hydroxide (caustic potash):  $K_2O + H_2O = 2KOH$ .

Two other oxides are known, namely, the dioxide ( $K_2O_2$ ) and the tetroxide ( $K_2O_4$ ), but they are comparatively unimportant substances.

**Potassium Chlorate** ( $KClO_3$ ) crystallizes in white tablets, is soluble in water to the extent of 3.3 per cent. at 0° C. and 59 per cent. at 100° C., and is largely used in the manufacture of explosives, percussion caps, matches, and pyrotechnics. It was originally made by the action of chlorine gas upon milk of lime and conversion of the resulting calcium chlorate into the potassium compound by interaction with potassium chloride and crystallization from the liquid. 'It is now manufactured 28\*

for the most part by the electrolysis of potassium chloride solution, the potassium hydroxide and chlorine generated in this way being mixed at a temperature of 70° C., thus producing the chlorate, which can be obtained from the solution by evaporation and crystallization.

It melts at from 360° to 370° C., and below 400° C. begins to decompose into potassium perchlorate and oxygen gas :



By careful regulation of the temperature, however, the evolution of oxygen gas can be avoided, in which case the decomposition is represented as follows:  $4\text{KClO}_3 = 3\text{KClO}_4 + \text{KCl}$ . Upon heating in the presence of a catalyst, such as finely divided manganese dioxide, oxygen is evolved. This reaction is in practice accompanied by the hazard of explosion if any organic matter, or free carbon or sulphur, happen to be present. The preparation of oxygen from potassium chlorate is not recommended. Potassium perchlorate may be used instead of the chlorate with comparative safety.

**Potassium Perchlorate** ( $\text{KClO}_4$ ) can be prepared from the chlorate as shown above, also from its continued electrolysis. It is only slightly soluble in cold water, but at 100° C. 20 parts pass into solution. When heated to between 450° and 600° C. it decomposes as follows:  $\text{KClO}_4 = \text{KCl} + 2\text{O}_2$ , and the velocity of change is facilitated by the presence of a catalyst, such as ferric oxide. This reaction is recommended for the preparation of small quantities of oxygen in the laboratory (see Oxygen).

**Potassium Carbonate** ( $\text{K}_2\text{CO}_3$ ) was originally obtained from the ashes of wood, hence the name "pot ashes," and is still extracted from this source in some parts of Canada and the U.S.A., where timber is abundant. A certain amount is made from the residue of beetroot molasses (see Molasses), but it is now chiefly made from potassium sulphate derived from the Stassfurt deposits by decomposition with calcium carbonate and carbon by a process resembling the old Leblanc soda process. It is soluble in water and used in the manufacture of soft soaps and glass, also for wool-washing. In the anhydrous form it is very deliquescent, and it forms a crystalline salt with water ( $\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ ). (See Ashes.)

**Potassium Bicarbonate** (**Potassium Hydrogen Carbonate, Potassium Acid Carbonate**) ( $\text{KHCO}_3$ ) is less soluble than potassium carbonate, and is used in making baking-powders. It is prepared by passing a current of carbon dioxide into a solution of the ordinary carbonate in water.

**Potassium Cyanide** ( $\text{KCN}$ ) is a white, deliquescent, soluble crystalline salt of very poisonous character, largely used as a solvent of gold in certain methods of extracting that metal from its natural sources, and in electroplating. (See Cyanogen, and Gold.)

**Potassium Cyanate** ( $\text{KCNO}$ ) is a white crystalline salt readily soluble in water and alcohol, and is used in a spraying solution to combat crab grass.

**Potassium Hydroxide** (**Caustic Potash**) ( $\text{KOH}$ ) can be prepared by

the action of slaked lime or milk of lime upon potassium carbonate solution, when calcium carbonate is precipitated and potassium hydroxide solution remains, as shown by the equation:  $K_2CO_3 + Ca(OH)_2 = CaCO_3 + 2KOH$ . Following upon filtration, the solution is concentrated by evaporation first of all in iron vessels, and finally to dryness and fusion in silver vessels. It is, however, for the most part now manufactured by the electrolytic method from potassium chloride. (See Sodium (Hydroxide).) It is a very deliquescent and caustic substance, and when dissolved in water, great heat is developed. It is used in soap-making, and in the textile and other trades, being prepared in various forms (lumps, sticks, liquid, and pellets), including a solid form of 88–90 per cent. and liquid form of 50° Bé.

**Potassium Nitrate (Nitre)** ( $KNO_3$ ), also known as saltpetre, is largely used as a fertilizer; also for pickling meat, in the manufacture of gunpowder, glass, enamels, and pyrotechnics. It is a white, crystalline salt, readily soluble in water, and is for the most part obtained from Chile nitre by steam-heating a solution of it in admixture with one of potassium chloride ( $KCl$ ), when a double decomposition occurs, expressed as follows:  $NaNO_3 + KCl = KNO_3 + NaCl$ . Under the working conditions of the process, most of the  $NaCl$  is precipitated in a crystallized form and removed, and the  $KNO_3$  is obtained later by crystallization of the mother-liquor and purification by recrystallization.

**Potassium Chloride, Bromide, and Iodide** ( $KCl$ ,  $KBr$ , and  $KI$ ) are all white, crystalline salts readily soluble in water. The chloride occurs in the water of the Dead Sea, but is prepared chiefly from the Stassfurt salt deposits in the form of concentrates, there being incidentally a wastage of magnesium chloride estimated at some 800,000 tons per annum. The chloride (muriate) is used as a fertilizer and in compounding some blasting explosives, as it lowers the flame temperature; in one form it is marketed of 80 per cent. strength.

The bromide can be prepared by the interaction of bromine and potassium hydroxide or from iron bromide and potassium carbonate, and, like the iodide, is used in photography and medicine.

The iodide is made, among other methods, by the action of iodine on potassium hydroxide and by precipitation of iron-iodide liquor with potassium carbonate and purification of the potassium iodide thus produced by crystallization.

**Potassium Fluoride** ( $KF$ ), made from potassium carbonate and hydrofluoric acid, forms a white, deliquescent, soluble hydrate with water ( $KF \cdot 2H_2O$ ), and finds some use in etching glass.

**Potassium Sulphides** include  $K_2S$ ,  $K_2S_2$ ,  $K_2S_3$ ,  $K_2S_4$ , and  $K_2S_5$ , all of which are soluble in water, and are decomposed by acids, evolving hydrogen sulphide ( $H_2S$ ), and liberating free sulphur in all cases except the first one. The monosulphide is obtained in red crystalline form of deliquescent character by reduction from the sulphate by heating with charcoal. The sulphides are used as depilatory agents.

**Potassium Sulphates**—The sulphate and bisulphate ( $K_2SO_4$  and  $KHSO_4$ ) are both colourless and crystalline, and to some extent

soluble in water, although not so soluble as most of the other potassium compounds. The ordinary sulphate (obtained by fractional crystallization from kainite and by action of sulphuric acid on potassium chloride) melts at  $1,072^{\circ}\text{C.}$ , is used in glass manufacture, also as a fertilizer, and in the preparation of alums. The bisulphate is used as a flux.

**Potassium Persulphate** ( $\text{K}_2\text{S}_2\text{O}_8$ ) is obtained by the electrolysis of a strong solution of potassium hydrogen sulphate in a divided cell, when, being sparingly soluble in water, it separates, and can be freed from the associated acid sulphate by recrystallization. It decomposes below  $100^{\circ}\text{C.}$ , and is a powerful bleaching and oxidizing agent.

**Potassium Sulphite** ( $\text{K}_2\text{SO}_3$ ) and potassium hydrogen sulphite ( $\text{KHSO}_3$ ) are crystalline salts soluble in water, both of which (particularly the latter) are used in the brewing industry and as sources of sulphur dioxide. (See Sulphites.)

**Potassium Metabisulphite** ( $\text{K}_2\text{S}_2\text{O}_5$ ) is a white, crystalline salt slightly soluble in water; used in pharmacy and as an antiseptic, its application being dependent upon its high available content of sulphur dioxide.

**Potassium Manganate and Permanganate** — See Manganese (Compounds).

**Potassium Acetate** ( $\text{K}(\text{C}_2\text{H}_3\text{O}_2)$ ) — A white, crystalline powder, soluble in water, used in medicine, etc.

**Potassium Citrate** ( $\text{K}_3(\text{C}_6\text{H}_5\text{O}_7)\cdot\text{H}_2\text{O}$ ) is a colourless, crystalline salt soluble in water and alcohol, and used in medicine.

**Potassium Dihydrogen Phosphate** ( $\text{KH}_2\text{PO}_4$ ) — A colourless, crystalline salt used as an acidic material in compounding baking-powders and in medicine.

**Potassium Bitartrate (Cream of Tartar)** ( $\text{KHC}_4\text{H}_4\text{O}_6$ ) is a white, crystalline, soluble salt, used as an acidic material in compounding baking-powders. (See Argol, and Tartar.)

**Potassium Sodium Tartrate (Rochelle Salt)** ( $\text{KNa}(\text{C}_4\text{H}_4\text{O}_6)\cdot 4\text{H}_2\text{O}$ ) — A colourless, crystalline salt which loses its water at  $215^{\circ}\text{C.}$  and is used as a depilatory and in medicine. With cupric salts it forms a complex cuprictartrate ion soluble in alkali (see Fehling's Solution).

**Potassium Thiocyanate (Sulphocyanide or Sulphocyanate)** ( $\text{KCNS}$ ) — A colourless, crystalline compound used in making freezing mixtures and artificial mustard oil. With ferric salts it forms a red solution, which is an important analytical test for ferric ion and for thiocyanate ion.

**Potassium Oxalate** ( $\text{K}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ ) is a colourless, crystalline salt, soluble in water; so also is the potassium hydrogen oxalate ( $\text{KHC}_2\text{O}_4\cdot\frac{1}{2}\text{H}_2\text{O}$ ) (sometimes called binoxalate and commonly known as "salt of sorrel") which is used for scouring metals and as a wood cleanser; and there is an acid potassium oxalate ( $\text{KHC}_2\text{O}_4\cdot\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$ ) (also known as tetroxalate). With calcium salts it forms a white solid, calcium oxalate ( $\text{CaC}_2\text{O}_4$ ), soluble in hydrochloric acid (high concentration of hydrogen ion), insoluble in acetic acid (low concentration of hydrogen ion), which is an important analytical test for calcium ion and for oxalate ion.

**Potassium Chromate and Dichromate** — See Chromium (Compounds).

**Potassium Ferricyanide (Prussiate of Potash (Red))** ( $K_3Fe(CN)_6$ ) is a crystalline, poisonous substance of blood-red colour, readily soluble in water, which forms with solutions of many compounds of the heavy metals, precipitates of characteristic colours; hence its use in dyeing and calico-printing when used alone, or with solutions of iron salts for the production of blue colours on wool and cotton; also used in connection with the discharge of indigo-blue colouring from calico and in the preparation of some pigments. It is made by the action of chlorine upon a solution of the yellow prussiate of potash or by its electrolysis.

**Potassium Ferrocyanide (Prussiate of Potash (Yellow))** ( $K_4Fe(CN)_6 \cdot 3H_2O$ ) is a crystalline, poisonous substance of lemon-yellow colour, readily soluble in water, made by heating a mixture of nitrogenous material such as dried blood, horn, and parings of hides with an equal weight of potassium carbonate and one-third of their weight of iron filings. There are other processes for making it respectively from the "spent oxide" from gasworks (containing cyanogen compounds), from thiocarbamide, and from calcium ferrocyanide by interaction with quicklime. It is manufactured on a large scale for use in dyeing and calico-printing, also in the preparation of Prussian blue and processes of electroplating and electrogilding.

Potassium compounds display a lavender colour when heated to volatilization.

**POTATO** (*Solanum tuberosum*, N.O. Solanaceæ) — Potato flour is used in the manufacture of starch, dextrine, glucose, etc., and as a wheat flour substitute. (See Starch.)

**POTATO SPIRIT** — See Fusel Oil.

**POTTERY** — See Porcelain.

**POWDER METALLURGY** — A technique for the fabrication of finished or semi-finished products by first compressing into shape under high pressures powder-mixtures prepared from metals, alloys, and in some cases non-metallic substances, and then sintering at temperatures well below the fusion point of the product. The importance of this technique lies in the fact that useful metal-like products exact in dimensions can be fabricated on a mass-production scale without melting, casting, or machining operations.

*References:* *A Course in Powder Metallurgy*, by W. J. Baeza (Reinhold Publishing Corp., New York); *Powder Metallurgy*, by P. Schwarzkopf (Macmillan Co., New York); *Principles of Powder Metallurgy*, by F. Skaupy (Philosophical Library, New York); *Powder Metallurgy*, by J. Wulff (American Society for Metals, Cleveland, Ohio); *Powder Metallurgy—Principles and Methods*, by H. H. Hausner (Chemical Publishing Co., Brooklyn, New York); *Principles of Powder Metallurgy*, by W. D. Jones (Longmans, Green and Co., New York and London); *Treatise on Powder Metallurgy*, 3 vol., by Claus G. Goetzel (Interscience Publishers, New York).

**POWER** is the rate at which mechanical energy is exerted. The economics of power as applied to chemical engineering is the subject of a paper by A. Gibb (*Ind. Chem.*, **4**, 159 (1928)), and in a presidential address to the Institution of Chemical Engineers (*Transactions*, 1928) he dealt with the economics and position of the chemical industries that depend at the present time upon electrical power as a decisive factor. (See "Some Chemical Aspects of Power Production from Mineral Fuels" by J. T. Ward (*Chem. and Ind.*, **48**, 547 (1929)); *Chemistry in Power Plant*, by W. H. Miles (E. Benn, London); *Power Resources of the World (Potential and Developed)*, published by the Executive Council of the World Power Conference; *Transactions of World Power Conferences*, as follows: *First*, London, 1924; Sectional Meeting, Basle, 1926; Fuel Conference, London, 1928; Sectional Meeting, Barcelona, 1929; Sectional Meeting, Tokio, 1929; *Second*, Berlin, 1930; Sectional Meeting, Scandinavia, 1933; Chemical Engineering Congress, London, 1936; *Third*, Washington, 1936; *Annual Reports of the Progress of Applied Chemistry* (Society of Chemical Industry); *Minerals Yearbook* (U.S. Bureau of Mines, Washington); Coal, Energy, and Fuels.)

**POZZOLANIC MATERIALS** — Volcanic ash. (See Cement.)

**Pr** — A symbol used for propyl ( $C_3H_7$ ) radical.

**PRASEODYMIUM (Pr) and its Compounds** — Atomic weight, 140.92.

See Elements for other data. One of the rare-earth elements and a member of the cerium group of the same, occurring in the earth *didymia* and *monazite sand*, and isolated by the electrolysis of its anhydrous chloride. It decomposes water. As an alloying element, it forms metallic compounds with such metals as aluminium, copper, gold, lead, magnesium, mercury, silver, and tin.

There are three **oxides**, namely, the dioxide ( $PrO_2$ ), the trioxide ( $Pr_2O_3$ ), which is greenish-white, and the tetroxide ( $PrO_4$ ), which is almost black.

Its salts include a **chloride** ( $PrCl_3 \cdot 7H_2O$ ) and a **sulphate** ( $Pr(SO_4)_3 \cdot 8H_2O$ ), both green in colour.

**PRECIPITATION** — A reaction in a solution that leads to the formation of an insoluble substance which settles out of solution is called a precipitation. For example:  $H_2SO_4 + BaCl_2 \rightarrow 2HCl + BaSO_4 \downarrow$ . The barium sulphate is insoluble in the solution and settles out as a precipitate. The process is called precipitation. The formation of a precipitate in a chemical reaction causes the reaction to go more nearly to completion in the direction of the formation of the precipitate.

A precipitate will form in any solution (except in rare cases of supersaturation) when the ionic product of the ions exceeds the solubility product of the insoluble compound. An example will illustrate the principle. The solubility product of barium sulphate is  $1 \times 10^{-10}$ . That is to say, the concentration of  $Ba^{++}$  ion expressed in moles per litre [ $Ba^{++}$ ] multiplied by the concentration of the sulphate ion expressed in moles per litre [ $SO_4^{--}$ ] is equal to  $1 \times 10^{-10}$  in a saturated solution. Stated by equation [ $Ba^{++}$ ]  $\times$  [ $SO_4^{--}$ ] =  $10^{-10}$  at  $25^\circ C$ . In

any solution at 25° C. containing barium ions and sulphate ions, regardless of the source, when the concentrations are such that their product is greater than  $10^{-10}$  there will be formed a precipitate of barium sulphate. On the other hand, if the product of the ion concentrations is less than  $10^{-10}$ , then no barium sulphate will precipitate.

**PREGNENINOLENE** — See Ethisterone.

**“PREGNYL”** — See Gonadotrophin.

**PREHNITE** — Hydrous silicate of alumina and lime, sometimes containing ferric oxide in substitution of part of the alumina, and probably derived from igneous rocks such as porphyrite; found in Scotland, Cape of Good Hope, etc.; crystal system No. 4, and sp. gr. about 2.8.

**PREMIER JUS** — See Oleo.

**PRESERVATIVES** — See Foods, Fruits, Silicon (Esters), and Stone Preservation.

**PRESSURE (High and Low)** — Pressure means the force, either push or pull, acting on unit area of surface. Pressure is a type of stress characterized by its uniformity in all directions. Pressure is usually associated with a decrease in volume. The opposite stress, accompanying an increase in volume, is referred to as a “negative pressure” or a vacuum.

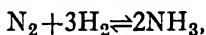
Pressure is expressed in a number of different units, namely, pounds per square inch; grams per square centimetre; bar or bayre (one dyne per square centimetre); millimetres, centimetres, or inches of mercury or some other liquid (the pressure equivalent to a column of the liquid of the height indicated acting on unit area); atmospheres (multiples of a unit pressure arbitrarily taken as 14.7 pounds per square inch, or 1,034 grams per square centimetre, or 76.0 centimetres of mercury at 0° C., which is equivalent to 1,013,246 bars).

In measuring pressure it is often convenient to take atmospheric pressure as an arbitrary zero point and to state the measured pressure in terms of positive and negative values. For example, an absolute pressure of  $\frac{1}{2}$  atm., 1 atm.,  $1\frac{1}{2}$  atm. would be expressed as  $-\frac{1}{2}$  atm., 0.0 atm., and  $+\frac{1}{2}$  atm. pressure on this relative scale. In speaking of pressures of less than one atmosphere absolute the term vacuum is often used. Thus an absolute pressure of 1 mm. of mercury pressure would be called a vacuum of 1 mm. of mercury. The term “negative pressure” is sometimes used in a comparative sense to indicate a pressure less than some predetermined reference pressure.

The term vacuum would indicate a system of low pressure approaching as a limit a region entirely devoid of matter (not energy). Because of diffusion and volatility this region is never attainable but remains merely as an ideal. In common usage the term vacuum indicates a low pressure range attained by some form of a pump. A pressure of one mm. of mercury would be called a vacuum, while a pressure of 0.0001 mm. would be called a high vacuum. The best vacuum attainable by artificial means is of the order of  $10^{-8}$  mm. of

mercury. It is conceivable that the closest approach to a perfect vacuum would be in inter-stellar space, but even so we must remember that energy is present.

The effect of pressure upon chemical change can be roughly predicted by the Le Chatelier principle, if neither extreme of the pressure scale is employed. In a gaseous system an increase in pressure will act in such a way as to favour the formation of substances on the reaction side that have the smaller volume. Conversely, diminishing the pressure will favour an increase in volume and the reaction will tend to shift to the side that has the larger volume. A classical example is the synthesis of ammonia gas from the elementary gases hydrogen and nitrogen; the reacting volumes follow the reaction equation:



where 1 volume of nitrogen plus 3 volumes of hydrogen of reactants (equalling 4 volumes total) yields 2 volumes of ammonia. Increase in pressure favours the formation of ammonia, whereas decrease in pressure favours the decomposition of ammonia. In industrial practice a pressure of 300 to 1,000 atmospheres is used.

If all the substances undergoing a chemical change are solutions or solids "normal" pressure (a few atmospheres) will have no appreciable effect upon the chemical reaction. On the other hand, if abnormal pressures, say in the vicinity of 1,000 to 20,000 atmospheres, are employed there is likely to be a noticeable effect upon the system.

Many physical transitions are accomplished by high pressure, such as liquefying gases below their critical temperature (see Matter), melting of ice, solidification of some liquids, and transitions between different solid forms of the same substance.

P. W. Bridgman of Harvard University has made many investigations of the effect of high pressure (up to 50,000 atmospheres) upon the properties of matter. Under sufficient pressure solid ice undergoes many transitions (about seven); one form of ice at about 20,000 atmospheres pressure is a solid at about 100° C.

At the Bell Telephone Laboratories quartz crystals of sufficient purity to be used in sound production and detection are produced at pressures in the vicinity of 1,000 atmospheres. Attempts have been made to produce diamonds by subjecting carbon to tremendous pressures generated by quenching steel into which excess carbon has been dissolved.

Low-pressure systems are utilized in many processes such as molecular distillations, vacuum distillation or separations, and cleaning surfaces for fine optical coatings. (See Pumps.)

A number of instruments are available to measure pressure (both relative and absolute). The ordinary mercury barometer is a convenient device for measuring pressures in the vicinity of atmospheric pressure. Its working principle is based upon measuring the height of a column of mercury, in an evacuated tube, maintained by a pressure acting on the mercury in the open arm of the tube. A convenient metallic barometer, called an aneroid, consists of an evacuated metallic

box containing a thin corrugated top which is supported internally by a spring. As the external pressure changes it causes slight movement in the top of the box, which motion is then greatly magnified by means of levers and a delicate chain, and is communicated to a pointer on a calibrated scale.

An open manometer is used to measure small differences in pressure between two systems. For greater sensitivity some liquid less dense than mercury is desirable. The principle involved here is one based upon the fact that the pressure in one system varies from the pressure in the other system by an amount equal to the pressure exerted by a column of the liquid equal in height to the differences between the two columns.

To measure very low pressures a closed-tube manometer or a McLeod gauge is used. The principle is based upon trapping a large volume of gas by mercury into a very small container terminating in a closed capillary tube. The height of the mercury column trapping the air is then compared with another column of mercury, from the same common pool of mercury, attached to the low-pressure system. The McLeod gauge can be used for measuring to  $10^{-4}$  mm. of mercury pressure.

For pressures greater than atmospheric pressure a tube of elliptical cross-section and sealed at one end is bent into a nearly complete circle. The open end of the tube is attached to the system whose pressure is being measured. As the pressure increases, the tube tends to straighten out and causes a pointer to move on a calibrated scale.

*References:* *Scientific Foundations of Vacuum Technique*, by Saul Dushman (John Wiley and Sons, New York); *Vacuum Manipulation of Volatile Compounds*, by R. T. Sanderson (John Wiley and Sons, New York); *The Design of High Pressure Plant*, by D. M. Newitt; "Vacuum Systems, Seals and Valves," by Kurie (*Rev. Sci. Instruments*, **19**, 485 (1948)); *High Vacua*, by Jnanananda (D. Van Nostrand Co., New York); *The Physics of High Pressure*, by P. W. Bridgman (G. Bell and Sons, London); 1936 Perkin Medal Address, by W. K. Lewis on "Applications of Physical Data to High Pressure Processes."

**PRESSURE (Atmospheric)** — See Air, and Barometers.

**PRESSURE (Critical)** — See Gases.

**PRESSURE (Vapour)** — See Vapour Pressure; and Water.

**PRESSURE DIE-CASTING** — See Die-Casting.

**PRICIETE** ( $3\text{CaO}, 4\text{BO}_3, 6\text{H}_2\text{O}$ ) — A boron mineral. (See Colemanite.)

**PRICKLY PEAR or INDIAN FIG** (*Opuntia*, N.O. Cactaceæ) — This fruit is used in South Africa as a source of industrial alcohol, motor fuel, and fuel for lighting and heating, while the by-products include vinegar, sugar, yeast, oil, and fruit jellies. Some 2,000,000 acres of land in South Africa are said to be infested with the common prickly pear, *O. vulgaris*, which is a native of parts of South America.

**PRIMULINES** — Dye-stuffs, being thiazole derivatives. (See Dyes.)

**PRINTER'S IRON LIQUOR** — See Iron (Ferrous Acetate).

**PRINTING INK** — See Inks.

**"PRIVINE"** — See Naphazoline Hydrochloride.

**PROCAINE (Ethocaine)** ( $C_{13}H_{20}O_2N_2$ ) — A synthetic base, namely, diethylaminoethyl-*p*-aminobenzoate ( $((C_2H_5)_2N.C_2H_4.OOC.C_6H_4.NH_2)(4)$ ). Procaine hydrochloride ("Novocaine") is a white, crystalline substance, soluble in water and in alcohol, m.p.  $154^\circ$  to  $156^\circ$  C. It is used in medicine as a local anæsthetic, having now largely replaced cocaine which is more toxic. The borate of the same base ("Borocaine") has also been used.

**PROCESS DEVELOPMENT** — The procedure whereby a new manufacturing process is transformed from a laboratory experiment to a profitable commercial undertaking. To advance directly from the laboratory to a full-sized manufacturing plant is a hazardous step, and one which is justified only where time is precious and cost no object (as in the development of the atomic bomb). The normal technique of process development is a combination of engineering calculations, commercial studies, and practical experiments on a gradually increasing scale. Opinions differ somewhat as to the exact order in which these should be undertaken, and the number of stages into which the development procedure is most conveniently divided. The modern trend is towards a more thorough preliminary study on paper before any practical experiments are made.

Barnebey (see below) recognizes six stages in process development : (1) *Laboratory Research* (yields, principal operating conditions) ; (2) *Product Evaluation* (markets, distribution, advantages over other processes, patents) ; (3) *Process Study* (large-scale laboratory work, unit processes required, tentative plant layout) ; (4) *Preliminary Engineering* (detailed engineering studies, flow sheets, heat and material balances, preliminary design of process units, plant location, raw materials, labour, services, legal aspects) ; (5) *Pilot Plant Study* (quantitative data for plant design, with special attention to novel equipment, materials of construction, effect of impurities, hazards, utility requirements—see Pilot Plant) ; (6) *Commercial Plant* (final design, accurate cost estimates, recheck of market analysis and production costs, operating instructions).

*References* : L. H. Baekeland in *J. Ind. Eng. Chem.*, **8**, 184 (1916) ; A. D. Little in *J. Soc. Chem. Ind.*, **48**, 202T (1929) ; H. L. Barnebey, in "Process Development" (*Trans. Amer. Inst. Chem. Eng.*, **40**, 559 (1944)) ; and Economic Aspects.

**PROCESS METALLURGY** — A division of metallurgy dealing with the extraction of metals from ores by chemical and physical operations. Several important steps are generally involved. The ores are first mined and concentrated (see Ores and Their Treatment). The sulphide-types are next roasted to oxides, and then reduced by smelting. The recovered metal is finally refined by either electrolytic, chemical, or distillation methods. (See individual metals for details.)

*References* : *General Metallurgy*, by H. O. Hofman (McGraw-Hill

## PROCESS METALLURGY — PROGUANIL HYDROCHLORIDE 883

Book Co., New York); *The Metallurgy of the Common Metals*, by L. S. Austin (John Wiley and Sons, New York); *Outline of Metallurgical Practices*, by C. R. Hayward (D. Van Nostrand Co., New York); *Ferrous Production Metallurgy*, by J. L. Bray (John Wiley and Sons, New York); *The Metallurgy of Iron and Steel*, by B. Stoughton (McGraw-Hill Book Co., New York); *Handbook of Non-ferrous Metallurgy*, Vols. I and II, by D. M. Liddell (McGraw-Hill Book Co., New York); *Non-ferrous Production Metallurgy*, by J. L. Bray (John Wiley and Sons, New York); *The Metallurgy of the Non-Ferrous Metals*, by W. Gowland and C. O. Bannister (Charles Griffin and Co., London); and *Engineering Metallurgy*, by B. Stoughton and A. Butts (McGraw-Hill Book Co., New York).

**“ PRODORITE ”** — A specially hard pitch-binder which can be moulded and reinforced like ordinary concrete; said to be very useful for dealing with the corrosive gases from superphosphate dens and for other kinds of acid-resisting chemical plant. It is described as a true concrete, free from plasticity, consisting of an aggregate of broken stone, sand, and a filler bound up with bitumen pitch. It has been otherwise described as concrete in which the Portland cement is replaced by from 7 to 12 per cent. of this special pitch.

**PRODUCER GAS** is made by passing air and steam over red-hot coke or coal, thus generating a mixture of carbon dioxide ( $\text{CO}_2$ ) and carbon monoxide ( $\text{CO}$ ), together with some proportion of hydrocarbons, the nitrogen contained in the air used, and hydrogen from the decomposed steam. It contains about 30 per cent. of carbon monoxide (any ammonia produced from the coal being washed out and recovered), and is largely used as a fuel gas for many manufacturing purposes on account of its cheapness. (See Carbon Oxides, Gas Producers, Mond Gas, Nickel, and Water Gas.)

**PROFLAVINE HEMISULPHATE** ( $(\text{C}_{13}\text{H}_{11}\text{N}_3)_2\cdot\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$ ) — An orange-red dye, being the neutral sulphate of 3, 6-diaminoacridine; soluble in water, sparingly soluble in alcohol, insoluble in chloroform and in ether. Used in medicine as an antiseptic. (See Acridine.)

**PROGESTERONE** ( $\text{C}_{21}\text{H}_{30}\text{O}_2$ ) — The hormone of the corpus luteum, namely, 3,20-diketo- $\Delta^4$ -pregnene, extracted from the corpus lutea of sow ovaries or prepared by oxidative degradation of cholesterol. It occurs as a colourless, crystalline solid; insoluble in water, soluble in alcohol and in vegetable oils; m.p.  $128^\circ$  to  $131^\circ\text{C}$ . It induces a secretory phase in the uterine endometrium, and, after fertilization, is instrumental in maintaining pregnancy. It is used in medicine, and is administered by injection as a sterile solution in a suitable vegetable oil. (See Corpus Luteum, and Ethisterone.)

**PROGUANIL HYDROCHLORIDE** (“ Paludrine ”) ( $\text{C}_{11}\text{H}_{16}\text{N}_6\text{Cl}\cdot\text{HCl}$ ) — A white, odourless, crystalline compound, namely,  $N^1$ -*p*-chlorophenyl- $N^5$ -isopropyldiguanide hydrochloride; slightly soluble in water; insoluble in organic solvents; m.p. about  $240^\circ\text{C}$ . It is used for the

prophylaxis and treatment of malaria. For a review of the chemotherapy used in the treatment of malaria, see N. Hamilton Fairley, *Brit. Med. J.*, **2**, 891 (1949). (See Chloroquine Diphosphate, Mepacrine, and Pamaquin.)

**PROLACTIN** — A hormone found in the pituitary gland of mammals, which stimulates the secretion of milk.

**PROMETHIUM** (Pm) — The name of element 61 accepted (1949) by the International Union of Chemistry, discovery credited (1945) to J. A. Marinsky and L. E. Glendenin of Oak Ridge Laboratory of the U.S. Atomic Commission. Promethium is a product of (1) uranium fission, and (2) neutron bombardment of neodymium; and its estimated atomic weight is 147.

“**PROMIN**” — A proprietary name for the sodium salt of *p,p'*-diaminodiphenylsulphone-*N,N'*-didextrose sulphonate, a white or pale yellow solid, soluble in water. It is one member of a series of sulphones which have been used clinically in the treatment of tuberculosis and leprosy but is not well tolerated when administered orally. It is less toxic but also less effective when injected intravenously. Results in the treatment of tuberculosis have been disappointing. For an account of its use in the treatment of tuberculosis, see Feldman *et al.*, *Proc. Mayo. clin.*, **15**, 695 (1940); Hinshaw *et al.*, *Amer. Rev. Tuberc.*, **47**, 26 (1943); **50**, 26 (1944); *Ann. Int. Med.*, **22**, 696 (1945). Results in the treatment of leprosy have been more encouraging, see Faget and Pogge, *Pub. Hlth. Rep.*, **60**, 1165 (1945). (See Diasone, “Promizole,” and “Sulphetrone.”)

**PROMINAL** — See Methylphenobarbitone.

“**PROMIZOLE**” — An organic compound, namely, 4,2'-diaminophenyl-5'-thiazolyl sulphone, used for the treatment of tuberculosis and leprosy. Its use in the former condition has proved disappointing but better results have been obtained in the treatment of leprosy, see Faget, *Pub. Hlth. Rep.*, **61**, 957 (1946). (See Diasone, “Promin,” and “Sulphetrone.”)

**PROMOTER** — See Activation, and Catalysis.

“**PRONTOSIL ALBUM**” — See Sulphanilamide.

**PROOF-SPIRIT** — Alcohol containing 49.28 per cent. real alcohol by weight, and 57.10 per cent. by volume, having a sp. gr. of 0.920 at 60° F. or 15.66° C.; every additional 0.5 per cent. alcohol above that being described as “1 degree over proof” (British practice). The factor for calculating proof spirit from volume percentage is 1.7535. As defined by the United States Government “proof spirit” is one containing 50 per cent. by volume of ethyl alcohol and 50 per cent. water, that is, 42.47 per cent. by weight of ethyl alcohol, and of density 0.930 at 20° C. compared with water at 4° C.

The term proof-spirit is a relic of the days when there was no ready method of determining alcohol content, an alcohol being considered under-proof if it contained so much water that gunpowder moistened

with it refused to burn, and over-proof if it did not prevent ignition. It followed that proof-spirit was a spirit of such a strength that it just allowed gunpowder to burn, the addition of a very small quantity of water rendering the spirit "not-proven," or under-proof. The test, although rough and ready, was one that could be easily carried out by uneducated Customs officials.

**PROOF STRESS** — The stress necessary to yield some predescribed permanent deformation in materials to establish their limitations in structural applications.

**PROPAMIDINE ISETHIONATE** ( $C_{21}H_{32}O_{10}N_4S_2$ ) — A white powder, being the di-( $\beta$ -hydroxyethanesulphonate) of 4,4'-diamidino- $\alpha$ ,  $\omega$ -diphenoxypropane; soluble in water and in alcohol, insoluble in chloroform and in ether; m.p. about 235° C. Used in medicine as an antiseptic.

**PROPANE** — See Hydrocarbons.

**PROPENYL** — The univalent radical or group  $CH_3\cdot CH:CH-$  (not to be confused with the allyl radical  $CH_2:CH\cdot CH_2-$ ).

**PROPIONIC ACID** ( $CH_3CH_2COOH$ ) — One of the normal fatty acids of small importance as a natural product, said to be contained in the products of wood distillation, also in coconut milk when turned sour, and in crude oil of amber. It is made by the oxidation of normal propyl alcohol with dichromate mixture, and is a colourless, oily acid, soluble in water and alcohol, with an odour something like that of acetic acid, of sp. gr. 0.992 and b.p. 141° C.

**PROPIONYL** — The acyl group,  $CH_3CH_2CO-$ , of propionic acid.

**PROPYL** — The monovalent radical group  $C_3H_7$  ( $CH_3CH_2CH_2-$ —(*normal*) or  $(CH_3)_2CH-$ —(*iso*)).

**PROPYL ALCOHOL** — See Alcohols, and Isopropyl Alcohol.

**PROPYLAMINE** — See Amines.

**PROPYLENE** — See Hydrocarbons (Olefines).

**PROPYLIDINE** — The divalent group  $CH_3\cdot CH_2\cdot CH<$ .

"**PROSTIGMINE**" — See Neostigmine.

**PROTACTINIUM** (Pa) — Atomic weight 231. See Elements for other data. Protactinium was recognized as a chemical element by the International Committee on Atomic Weights in 1937, and this spelling, rather than protoactinium, accepted (1949) by the International Union of Chemistry. It is a radioactive element of the actinium series, a homologue of tantalum, and precipitable with zirconium phosphate. A. V. Grosse discusses this element in *J. Amer. Chem. Soc.*, **52**, 1742 (1930), and Grosse and Agruss describe its technical extraction in *Ind. Eng. Chem.*, **27**, 422 (1935).

**PROTAMINES** — Strongly basic, water-soluble proteins, occurring in ripe fish sperm.

**"PROTARGOL"** — A protein compound of silver, soluble in water and glycerol, used as an antiseptic and in medicine. (See Silver Protein.)

**PROTEIDS** — Proteins (see same).

**PROTEINS** — The name given to those substances forming the bulk of living tissues, such as the protoplasm of all living cells, hair, horn, etc., and making up, together with fats and carbohydrates, almost the entire structure of all biological types. All proteins contain carbon, hydrogen, oxygen, and nitrogen, and the majority contain sulphur, while phosphorus is of quite common occurrence. On hydrolysis all yield a mixture of amino-acids as final products, while partial hydrolysis yields simpler bodies such as metaproteins, proteoses, peptones, and polypeptides, the latter being simple substances easily synthesized from amino-acids by condensing the amino group of one with the acid group of a second, so as to yield compounds containing the grouping  $\text{—CO.NH.CH—}$ , which is characteristic of proteins and all their hydrolytic products. This type of grouping renders proteins amphoteric in their nature, so that the majority are soluble in strong acids and also in alkalis, but they tend to come out of solution at a definite hydrogen-ion concentration, the  $pH$  at which precipitation most readily occurs being known as the isoelectric point. This differs in the case of most proteins, and forms an important means of separation, *e.g.*, in the preparation of insulin of high potency.

Owing to their unstable nature proteins are isolated with difficulty in the crystalline state and their approximate molecular weights determined; that of the enzyme pepsin has been found to be of the order of 35,000–39,000.

Proteins cannot be directly assimilated into the metabolism of any organism, owing partly to their large molecular weights which render them not readily diffusible, and partly to their great specificity, *i.e.*, different proteins are found in the tissues of different animals. In the body they are hydrolysed to their constituent amino-acids, and the latter synthesized into different proteins by enzymes, themselves protein in nature. Proteins alien to the organism can be very toxic when introduced parenterally, the best-known examples of this phenomenon being the bacterial toxins, most of which are proteins. Other proteins of biological importance are insulin, hæmoglobin, all the enzymes, and some of the hormones.

*References* : The system of classification of proteins adopted by the American Society of Biochemists is given in the article on "Amino-acids, Polypeptides, and Proteins" of *Van Nostrand's Scientific Encyclopedia* (D. Van Nostrand Co., Inc., New York), and the ordinary English one in Bernthsen's *Organic Chemistry* (Blackie and Son, London); table giving the percentages of some amino-acids derived from various proteins, by S. Dixon (*Chem. and Ind.*, 49, 664 (1930)); *Animal Proteins*, by H. G. Bennett (Baillière, Tindall and Cox, London); *Chemistry of the Proteins*, by Dorothy J. Lloyd (J. and A. Churchill, London); *The Chemistry of the Aminoacids and Proteins*, by C. L. A. Schmidt (C. C. Thomas, Baltimore); *Outline of the Amino*

*Acids and Proteins*, by M. Sahyun (Reinhold Publishing Corp., New York); *Chemistry and Biology of Proteins*, by Felix Haurowitz (Academic Press, New York); *Albumins, Biochemistry, Enzymes, Foods, and Polypeptides*.

TABLE SHOWING PERCENTAGES OF VARIOUS ALPHA-AMINO-ACIDS IN CERTAIN PROTEINS.

Alpha-Aminoacid		Gliadin of Wheat Per Cent.	Zein of Corn Per Cent.	Milk Albumin Per Cent.	Casein Per Cent.	Egg Albumin Per Cent.
Glutamic acid	5 Carbon atoms	44	31	13	22	13
Arginine	Guanidine derivative	3	2	3	—	6
Phenylalanine	Benzenoid derivative	2	8	1	4	5
Tyrosine	Benzenoid and Phenolic derivative	3	6	2	7	4
Cystine	Sulphur- containing	2	1	4	—	1
Tryptophane	Benzenoid derivative	1	—	3	—	1
Proline	Pyrrolidine derivative	—	13	—	—	—
Leucine } Isoleucine }	6 Carbon atoms	—	—	—	—	25

**PROTEOSES** — Products of the hydrolysis of proteins, precipitated by ammonium sulphate. (See Albumins, and Proteins.)

**PROTO-** — A prefix meaning "first."

**PROTOACTINUM** — See Protactinium.

**PROTocatechuic Acid** ( $C_6H_3(OH)_2COOH$ ) — A colourless crystalline substance soluble in water, made by heating catechol ( $C_6H_4(OH)_2$  (1, 2)) with ammonium carbonate; used in photography.

**PROTON** — The positive nucleus of the hydrogen atom, of mass 1800 times the mass of the electron, and of unit positive charge. Nuclei of the elements heavier than hydrogen contain whole number multiples of the proton. Identified by Rutherford in 1920. (See Acids, Atoms, Electrons, Elements, Energy, and Nuclear Chemistry.)

**PROUSTITE** — A mineral, double sulphide of silver and arsenic ( $3Ag_2S, As_2S_3$ ) found in Arizona, New Mexico, etc. (crystal system No. 3, and sp. gr. 5.4 to 5.6).

**PRUSSIAN BLUE (Ferric Ferrocyanide)** ( $Fe_4(Fe(CN)_6)_3$ ) — The name of a blue pigment used in dyeing and making inks and paints, made from potassium ferrocyanide and ferric salts. There are various methods available for making the several varieties of Prussian blue (Chinese "Milor" and "bronze blues"), varying with the nature of the raw materials from which the ferrocyanide is obtained. but they may be

stated to be based generally upon the action of potassium chlorate and sulphuric acid on a mixture of potassium ferrocyanide and ferrous sulphate in hot solution. A soluble blue, having the formula  $KFe(Fe(CN)_6)$ , has been described. There is also a process for making Prussian blue from coal gas containing cyanogen, by its action upon solutions of ferrous salts, hydrocyanic acid of the coal gas reacting to form Prussian blue. It may also be obtained by the electrolysis of a solution of potassium ferrocyanide, using an anode of iron. It is used in making Brunswick greens and chrome yellows, and is liable to take fire in grinding some mixtures, the ignition temperature of the pure substance being  $234^{\circ}C$ . A mixture of 20 per cent. Prussian blue and 80 per cent. lead chromate decomposes explosively at  $238^{\circ}C$ . Prussian blue dissolves in solutions of the normal alkali oxalates, giving greenish-coloured solutions, and loses its colour in the presence of sodium hydroxide solution. (See Potassium (Compounds), and Turnbull's Blue.)

**PRUSSIAN GREEN** (possibly  $K_6Fe_2(CN)_{12}$ ) is prepared by the long-continued action of chlorine upon potassium ferrocyanide.

**PRUSSIATES** — See Cyanogen, Carbonyl Ferrocyanides, and Potassium (Compounds).

**PRUSSIC ACID** — See Hydrocyanic Acid.

**PSEUDO COMPOUNDS** may be generally described as those which approximate in some manner or measure better recognized types; thus the tautomeric forms of certain nitro compounds are known as pseudo-acids, for example, phenylnitromethane ( $C_6H_5.CH_2NO_2$ ) forms a sodium salt; so there are pseudo-alums, pseudo-morphs, pseudo-solutions, and so on.

**PSYLLIUM SEED (Flea Seed)** — The dried ripe seeds of *Plantago Psyllium* and *P. arenaria*, occurring in France, Spain, and Italy and grown in the U.S.A. It contains mucilage as its principal constituent and is used in medicine as a remedy for constipation.

**PTOMAINES (Toxins)** are basic bodies or alkaloids resulting from the putrefaction or metabolic decomposition of albuminoids (animal proteins). Reference to some of these, including putrescine and cadaverine, is made elsewhere. The resulting bases corresponding to nearly all the known amino-acids have been isolated. Phenylethylamine ( $C_6H_5CH_2CH_2NH_2$ ) may be viewed as typical, and is derived from the amino-acid phenylalanine ( $C_6H_5CH_2CH(NH_2)COOH$ ). A base named sepsine which produces symptoms of ptomaine poisoning in dogs, has been obtained from putrefied yeast. Some, but not all, ptomaines are of toxic character, and they are not all poisonous when taken by the mouth, but food infected by *B. botulinus* is poisonous.

A tainted odour is not a safeguard against the common and dangerous form of food-poisoning caused by the *Salmonella* group of bacteria; at the same time putrid food is not necessarily poisonous, as evidenced by the preference and immunity observed by many persons for "high" game. (See Albumins, Bacteria, and Toxins.)

**PTYALIN** — See Saliva.

**PUCHERITE** ( $\text{BiVO}_4$ ) — A rare mineral vanadium compound of bismuth (crystal system No. 4, and sp. gr. 6.25).

**PULEGONE** ( $\text{C}_{10}\text{H}_{16}\text{O}$ ) — A terpene ketone isomeric with camphor, and occurring in oil of pennyroyal and oil of pimento. It adds on one molecule of  $\text{HCl}$  to yield the so-called hydrochloride, but this, like dipentene hydrochloride, is merely the addition to an ethylenic link and does not indicate any basic properties in the molecule of the ketone, neither is the chlorine ionizable. Hence the compounds formed by terpene derivatives with  $\text{HCl}$  are not hydrochlorides, and the name should not be applied to such addition products.

**PULP** — See Paper.

**PULVERIZED FUEL** — See Coal, and Fuel (Powdered).

**PULVERIZERS** — See Grinding.

**PUMICE-STONE** — A cellular or very porous lava of volcanic production, probably derived from felspar, which floats in water, and is composed largely of silicate of aluminum. In a finely powdered state it is used as an abrasive, also in compounding scouring preparations, and as a base for carrying catalysts. The seat of the Italian pumice industry is the volcanic island of Lipari.

**PUMPS** — The principal types are Reciprocating, Centrifugal, and Positive Rotary. Reciprocating pumps are particularly suitable for high pressures and moderate rates of flow; centrifugal pumps can be built for either high or low pressures, but are better adapted for high rates of flow; positive rotary pumps are suitable for medium pressures and small or moderate rates of flow, more especially where a continuous flow is required rather than the pulsating delivery of a reciprocating pump.

Centrifugal pumps differ from other types in that the rate of pumping is not fixed by the speed; the flow can be partly or wholly shut off without harm while the pump is running. Such a proceeding would be liable to damage the mechanism of a reciprocating or positive rotary pump. Centrifugal pumps are therefore particularly suitable where the flow of liquid is to be automatically regulated by a control valve in the delivery line. The performance of a centrifugal pump conforms approximately to a *characteristic equation* of the type:

$$aN^2 + bNQ - cQ^2 = H,$$

where  $N$ =number of revolutions per minute,  $Q$ =gallons per minute,  $H$ =feet total head,  $a$ ,  $b$ , and  $c$ =constants for a given pump. The constants may be determined from tests at three different heads or speeds.

Centrifugal pumps are not normally self-priming, but have to be filled with liquid before they will start pumping. The maximum practicable head for a single impeller is about 300 feet. Centrifugal

pumps for higher pressures are therefore built with a number of impellers on one shaft (multi-stage pumps).

Reciprocating pumps may be of either the piston or the plunger type. Plunger pumps are more costly, but they have the advantage that the packing between cylinder and moving element can be changed or adjusted without dismantling the pump. They are often preferred for high pressures. Reciprocating pumps are also classified as steam or power according as the piston or plunger rod is directly coupled to a steam piston or driven through a connecting-rod and crankshaft. Steam pumps are cheaper and more flexible than power pumps, but their delivery rate is less uniform. The volumetric efficiency of reciprocating pumps (volume of liquid delivered *divided by* volume swept by piston or plunger) may vary from 50 to 99 per cent. High speeds and leaky valves or packing cause low volumetric efficiency.

A common type of positive rotary is the gear pump. It is cheap and simple in construction, but must have very close clearances between gears and casing if it is to operate efficiently. On the other hand, there should be a moderate degree of backlash between the gears themselves. Other types of positive rotary pumps have lobed impellers or eccentric drums with spring-loaded sliding blades.

Pumps are made in a great variety of materials, such as corrosion-resisting metals and alloys, plastics, and stoneware, to meet the various needs of the process industries. Most of the non-metallic materials are suitable for low pressures only. (See Air Lift.)

The "Sprengel" pump is an appliance in which mercury running down a narrow tube is used instead of water, and by its means the pressure may be reduced to 0.001 mm. of mercury. The "Gergk" pump of piston type, having valves immersed in oil, gives a vacuum of 0.0002 mm. The "Töpler" mercury pump is said to produce a vacuum of 0.00001 mm. of mercury, and when coupled with the use of charcoal to assist in the absorption of any remaining gas in the vessels to be exhausted, an enormously enhanced result is attained. Even greater claims are made on behalf of the "Gaede" pistonless pump, which gives a vacuum of 0.0000002 mm. By an arrangement in which liquid air and charcoal are used in association the degree of exhaustion reaches to 0.0000008 mm. of mercury. With a backing pump giving a vacuum of 0.2 mm. the new "Vitreosil" mercury condensation pump is said to give a vacuum of 0.000002 mm. quickly and readily.

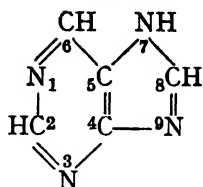
*References:* Standard works listed under Chemical Engineering; N. Swindin, *Modern Theory and Practice of Pumping* (Benn, London); "Pumps," by C. W. Cuno (*Ind. Eng. Chem.*, **24**, 1109 (1932)).

**PUNNA OIL**, from *Calophyllum Wightianum* (Wall) from the West Coast of Africa, is stated to contain glycerides of the same type as those found in cottonseed and sesame oils; it is of greenish-yellow colour, with a sap. v. of 187; i.v. (Winkler), 102.

**PURAPURIN** — See Glycosides.

**PURINE GROUP** — A number of bases, being derivatives of purine

( $C_5H_4N_4$ ), including caffeine and theobromine; also so-called cyclic diureides, including uric acid. Purine



is crystalline, colourless, and of m.p.  $216^{\circ}C$ .

Apart from such long-known compounds as caffeine, theobromine, theophylline, uric acid, adenine, and xanthine, the purines are of additional importance since it has been shown that they are essential constituents of certain enzymes, such as the co-enzymes I and II, and also of the essential nucleic acids. Although containing nitrogen, and often referred to as alkaloids, caffeine and the other purine bases have only very feeble basic properties, and are not strictly alkaloids.

**PURPLE OF CASSIUS** — A purple-coloured body obtained in the form of an impalpable precipitate by adding a solution of stannous chloride to a solution of gold, or by adding a neutral solution of gold chloride to one of the mixed stannous and stannic chlorides. A purple of fine tint is produced when the tin chloride is first of all added to a solution of ferric chloride until a shade of green is obtained, and then adding this mixture very gradually to a solution of gold chloride. The precipitate, when collected and dried, forms the so-called purple of Cassius, which is used as a colouring material in the red glass of Bohemia and for colouring enamels; it is regarded by Huber as a mixture of colloidal gold and colloidal stannic acid.

**PURPLE OF TYRE** — See Tyrian Purple.

**PURPURIN (1, 2, 4-Trihydroxyanthraquinone)** — A red colouring matter, being a valuable dye extracted from madder by the same process as alizarin, and separated therefrom by its greater solubility in alum liquor. From strong alcohol it crystallizes in red needles. It is more soluble in water than alizarin, and is produced synthetically from anthracene.

**PUS** — Creamy matter resulting from inflammation of wounds, and found in abscesses, consisting of serum and degraded tissue, crowded with white corpuscles (leucocytes) which have undergone degenerative change, and generally accompanied with abundant micrococci and bacteria. (See Albumins, and Ptomaines.)

**PUTREFACTION** — The expression by which is indicated a number of hydrolytic and other chemical changes in animal and vegetable compounds brought about by the action of microbes. (See Albumins, Bacteria, Microbes, Ptomaines, and Pus.)

**PUTTY** — A mixture of whiting (calcium carbonate) and 18 per cent. linseed oil, with or without added white-lead. Mixtures of pure calcium carbonate and acid-free linseed oil are devoid of plasticity, but the necessary gel structure can be secured by the incorporation of about 1 part in 10,000 alumina, or iron oxide.

**PUTTY POWDER** — Impure stannic oxide, containing about 25 to 50 per cent. of that substance, with from 71 to 46 per cent. of lead oxide, and 4 per cent. of impurities; used in enamelling and for polishing stone and glass. (See Tin (Oxides).)

**PYCNOMETER (Pyknometer)** — A glass vessel standardized to determine the specific gravities of liquids by weight.

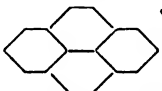
**"PYELECTAN"** — See Iodoxyl.

**"PYELOSIL"** — See Diodone.

**PYOCYANINE** — The blue pigment produced by *Bacillus pyocyaneus* of formula  $C_{26}H_{24}O_2N_4$ .

**"PYRALIN"** (Du Pont) — Trade-mark for cellulose nitrate thermoplastic material. Possesses notable toughness, resistance to moisture, and easy machinability.

**PYRARGYRITE** — A natural compound of antimony and silver sulphides ( $Ag_3SbS_3$ ), mined in the United States of America and New Mexico (crystal system No. 3, and sp. gr. about 5.8).

**PYRENE** ( $C_{16}H_{10}$ ; ) — A crystalline hydrocarbon of

m.p. 150° C. accompanying chrysene, etc., contained in the distillate from coal tar coming over above 360° C.

The same name is given to a make of fire extinguisher using carbon tetrachloride.


**PYRETHRUM (Insect Powder)** — The dried unexpanded flower heads of several species of *Chrysanthemum* (*Pyrethrum*), including *C. roseum*, *C. Marshalli* (*P. carneum*), and *C. cinerariaefolium*, when reduced to a fine powder are widely used as insecticides. In the United States the term "Insect Powder" legally may be applied only to preparations made from these species. Formerly grown in Dalmatia and later in Japan, the centre of the pyrethrum-raising industry is now in Kenya.

The active principles of pyrethrum are esters, of which four have been isolated: Pyrethrin I and II, and Cinerin I and II. These esters are oily liquids, insoluble in water, but soluble in a number of organic solvents. For insecticidal use the ground flower heads may be used as a dust or in water suspension, or, more commonly, a light petroleum oil extract may be used as a household insect spray. Such sprays are widely used under a variety of trade-names for the control of houseflies, mosquitoes, gnats, etc. Pyrethrum, although highly toxic to insects, is relatively non-toxic to higher animals, and hence finds favour for use in controlling insects on food crops, in eating establishments, and similar places.

*References:* *Pyrethrum Flowers*, Second Edition and supplement, by Gnadinger (McLaughlin Gormley King, Minneapolis); *Chemistry of Insecticides and Fungicides*, by D. E. H. Frear (D. Van Nostrand Co., New York); *Scientific Principles of Plant Protection*, by Martin (E. Arnold, London); and *Insecticides*.

**PYRETOL (Pyrethrin)** — A name sometimes given as that of the active principle of pyrethrum—very poisonous to cold-blooded animals. (See Insecticides, and Insect Powder.)

“**PYREX**” — See Glass.

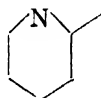
**PYRIDINE** ( $C_5H_5N$ ; ) — A practically colourless, liquid, basic

substance of penetrating, sharp odour, contained in tar oil, and present also in tobacco smoke; sp. gr. 0.982, b.p.  $115^{\circ}C.$ ; soluble in water, alcohol, ether, benzol, etc. It can be extracted in association with some of its homologues from the lower-boiling fractions of tar distillates, after removal of the tar acids, by agitation with sulphuric acid in which they dissolve, and in a pure state by heating its carboxylic acid with lime. It is used to some extent as a remedy for asthma, a denaturant for alcohol, and as a valuable solvent in the rubber, paint, and other industries. Chemically it has a heterocyclic ring constitution in which nitrogen replaces a carbon and a hydrogen of benzene.

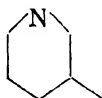
The pyridine derivatives exhibit isomerism similar to the benzene derivatives. (See *The Chemistry of Heterocyclic Compounds*, by A. A. Morton (McGraw-Hill Book Co., New York).) (See Picolines.)

**PYRIDOXINE** — See Vitamins.

**PYRIDYL** — The univalent radical  $C_5H_4N$  having a similar relation to pyridine as phenyl to benzene. According to the position of the substituent they are known as



alpha



beta



gamma

**PYRITES** — The mineralogical name of a number of natural compounds consisting of sulphides (chiefly iron and copper). There is a large consumption of pyrites in connection with the manufacture of sulphuric acid. In 1913 Europe provided 90 per cent. of the total production, Spain and Portugal furnishing 60 per cent., Norway ranking next, while Italy and France produced considerable quantities. Smaller amounts are mined in Roumania, Ireland, and Cornwall. (See Sulphur for World Production.)

Iron pyrite ( $FeS_2$ ) (crystal system No. 1, and sp. gr. about 5.0) exists in many countries and in several varieties. A large proportion of pyrites is so-called cuprous pyrite ( $Cu_2S, Fe_2S_3$ ) (crystal system No. 2, and sp. gr. about 4.2). Many are of arsenical character; one of them, named *mispickel*, has the composition  $FeAs_2, FeS_2$ , and others contain a notable quantity of nickel.

The gold, silver, and copper contained in pyrites used in the sulphuric acid manufacture are recovered from the burnt ore. The Rio Tinto iron pyrite contains about 50 per cent. sulphur, 40 per cent.

iron, from 1.5 to 3.8 per cent. copper, and 1 oz. 4 dwts. of silver per ton ; the Tharsis pyrite, about 3.5 per cent. copper and 15 dwts. silver ; and the San Domingo (Mason's), about 3.7 per cent. copper and 15 dwts. of silver. In the recovery of the copper great care has to be taken to first of all get rid of the arsenical constituent. In the " Freeman " flash roasting process for production of  $\text{SO}_2$  the pyrites are suspended in air, in the burning reaction. (See Copper, Iron, and Pyrrhotin.)

**PYRO** — A prefix denoting high-temperature determination instruments ; also some products, for instance, pyrogallol, pyroligneous acid and other substances derived from dry distillations. Pyrophosphoric acid is  $\text{H}_4\text{P}_2\text{O}_7$ . (See Pyrometers.)

**PYROCATECHOL (Pyrocatechin ; Ortho-dihydroxybenzene)** — See Catechol.

**PYROGALLOL (Pyrogallol ; Trihydroxybenzene)** ( $\text{C}_6\text{H}_3(\text{OH})_3$ ) (1, 2, 3) can be obtained from gall nuts, but better by heating gallic acid ( $\text{C}_7\text{H}_6\text{O}_6$ ) with water in an autoclave, thus eliminating carbon dioxide. It is a white, crystalline, trihydric phenol of the monoclinic-prismatic class, m.p.  $133^\circ\text{C}$ ., and can be sublimed without decomposition ; is soluble in water, and is a powerful reducing agent for silver salts, which gives it a use in photography as a developer. Dissolved in alkali, it has a great affinity for oxygen and is much used in gas analysis. With a solution of a ferrous salt it produces a beautiful indigo colour. Commercial samples exhibit a m.p. of from  $125^\circ$  to  $132^\circ\text{C}$ . (See Tannins.)

**PYROLIGNEOUS ACID** — The crude acetic acid liquor obtained, in association with tar, creosote, naphtha, and other products, by the dry distillation of wood, and from which it has to be separated ; after which it is neutralized by lime, and the calcium acetate thus obtained is then distilled with hydrochloric or sulphuric acid, yielding the acetic acid as distillate. (See Acetic Acid, and Wood (Distillation).)

**PYROLUSITE** — Mineral Manganese Dioxide.

**PYROLYSIS** — Process of chemical change effected by heat. The pyrolysis of carbon compounds is the subject of a monograph by C. D. Hurd (Reinhold Publishing Corp., New York). (See Petroleum (Cracking), Coal (Carbonization), and Wood (Distillation).)

**PYROMETER** — An instrument for measuring high temperatures by means other than the expansion of a fluid. The three principal types are thermo-electric, resistance, and optical. The first depends upon the electromotive force (E.M.F.) generated when a junction of dissimilar metals is heated. The E.M.F. varies with the temperature difference between the hot and cold junctions, and is measured by a galvanometer or potentiometer. In the resistance pyrometer a coil of wire is subjected to the temperature to be measured and its resistance determined by some form of Wheatstone bridge.

In optical pyrometers the intensity of light of a given wave length emitted from an incandescent body is matched against a variable

standard, *e.g.*, an electrically heated filament the temperature of which can be varied by means of a rheostat calibrated in temperatures. Observation may be visual or by means of a photo-electric cell. Optical pyrometers are suitable for temperatures up to  $3,000^{\circ}\text{C}$ . (See *Pyrometers*, by E. Griffiths (Sir Isaac Pitman and Sons, London); *Heat (Temperatures)*; *Instrumentation*; and *Thermometers*.)

#### MAXIMUM TEMPERATURES FOR PYROMETER ELEMENTS

Type	Material	Max. Temp. $^{\circ}\text{C}$ .
Thermo-electric	Cu-constantan	300
	Fe-constantan	850
	Chromel-alumel	1,200
	Pt-(Pt+Rh)	1,600
	W-Mo (in $\text{H}_2$ )*	2,000
Resistance	Copper	150
	Nickel	300
	Platinum	1,000

\* D Binnie, *J. Roy. Tech. Coll. Met. Club, Glasgow*, 6, 35, 42 (1927-8).

**PYROMORPHITE (Green Lead Ore)** ( $3\text{Pb}_3\text{P}_2\text{O}_8, \text{PbCl}_2$ ) — A natural lead compound (chloride-phosphate) found in some of the U.S.A.; crystal system No. 3; and sp. gr. 6.5 to 7.0.

**"PYRONIUM"** — A proprietary opacifying substitute for tin oxide, used in making enamels, 3 per cent. of which and 3 per cent. of tin oxide give better results, it is claimed, than 8 per cent. of tin oxide alone in leadless enamels, and is much cheaper.

**PYROPHORIC ALLOYS** — These include ferro-cerium, "Auermetal" (an alloy of iron and "misch metal"), and "Kunheim" (a misch metal). (See Iron (Alloys).)

**PYROPHORUS (Pyrophoric)** — The characteristic of materials which readily fire upon exposure to air, such as finely divided iron, cobalt, and nickel, as obtained from their oxides by reduction with hydrogen. The large surfaces thus exposed tend to rapid oxidation, attended with a large generation of heat sufficient to bring about incandescence.

**PYROPHYLLITE (Pencil Stone)** — A mineral hydrous aluminium silicate ( $\text{Al}_2\text{O}_3, 4\text{SiO}_2, \text{H}_2\text{O}$ ) somewhat like talc; used for making slate pencils, also as a ceramic raw material, and in the manufacture of "talcum" toilet powders.

**PYROTECHNY** — See Fireworks.

**PYROXYLIN** is typical of a number of substances used in competition with oil products, in the preparation of artificial leather cloth, lacquers, enamels, book-binding materials, and oil varnishes, and consists of a solution of nitrated cellulose in a solvent of comparatively high boiling-point, at times mixed with castor oil, linseed oil, or nitrated castor oil to impart body and flexibility to the product.

So-called "finishes" or colouring matters are employed in perfecting these articles, such as "Coricol."

The solvents comprise ethyl, butyl, and amyl acetates, various

alcohols, acetone, benzol, etc., diethyl carbonate, tricresyl phosphate, etc., and are used as plasticizers and stabilizers; various resins and pigments are also often incorporated in preparing pyroxylin lacquers and compositions.

Pyroxylin is a form of gun-cotton nitrated to the extent only of from 11 to 12.5 per cent. (in contrast with the explosive gun-cotton, which is nitrated to a higher degree), and thus is insoluble in some of the usual solvents. (See *Pyroxylin Enamels and Lacquers*, by S. P. Wilson (Constable and Co., London); Cellulose, Collodion, Dopes, Explosives (Gun-cotton), Lacquers, Nitrocellulose, Plasticizers, and Varnishes.)

**PYRRHOTIN (Pyrrhotite)** — Magnetic pyrites of varying composition and crystalline character found in many districts.

**PYRROLE**  $\left( \begin{array}{c} \text{HC}-\text{CH} \\ \parallel \quad \parallel \\ \text{C}_4\text{H}_4\text{NH}; \text{HC} \quad \text{CH} \\ \quad \quad \quad \backslash \quad / \\ \quad \quad \quad \text{NH} \end{array} \right)$  — A secondary base that is a con-

stituent of bone oil and coal tar. It is a yellowish, sublimable, liquid, basic body, soluble in alcohol and ether; sp. gr. 0.948, and b.p. 131° C. (See *The Chemistry of Heterocyclic Compounds*, by A. A. Morton (McGraw-Hill Book Co., New York).)

**PYTHAGORAS MASS** — See Porcelain.

**QUADRIVALENT (Tetravalent)** — See Valencies.

**QUALITATIVE ANALYSIS** (see also Analytical Chemistry) — That part of analytical chemistry dealing with the ways and means of ascertaining the nature of the constituents of matter is called qualitative analysis. The detection, identification, and estimation of substances depend upon inventing methods to cope with gases, liquids, solids, with active and inactive and with similar and dissimilar substances. The greater the differences in chemical behaviour, the easier it is in general to bring about a qualitative separation.

Much information can be gained by such simple preliminary examinations as those concerned with colour, odour, general and detailed appearance, hardness, density, solubility, behaviour on heating without free access to air: melting, boiling, sublimation, transition, or decomposition point, if any.

The accepted system of qualitative analysis in which 23 metals are separated and identified in solution of their nitrates will illustrate the principles under consideration. In the accompanying table 23 metallic ions are arranged in order of their group separations. The reactions used in separating each group are indicated.

The groups are separately treated for the final identification for presence or absence of each member by use of reactions whose effectiveness in separation and identification have been found to be satisfactory in each case.

The non-metallic or anion radicals of inorganic salts have been grouped for separation in the following way :

*Group I* : Silver nitrate produces a precipitate insoluble in nitric acid, and barium chloride produces no precipitate : chloride, bromide, iodide, cyanide, hypochlorite, ferrocyanide, ferricyanide, thiocyanate.

*Group II* : Silver nitrate produces a precipitate which is soluble in nitric acid, and barium chloride produces no precipitate : sulphides, tellurides, selenides, nitrites, acetates, cyanates.

TABLE SHOWING A SYSTEM OF QUALITATIVE ANALYSIS FOR METALLIC IONS

Analytical Group Number	Metals of the Group	Precipitate	Reaction used for Group Separation
I	Lead Mercurous Silver	PbCl <sub>2</sub> , white Hg <sub>2</sub> Cl <sub>2</sub> , white AgCl, white	Hydrochloric acid added to the cold solution. Lead chloride is not completely removed.
II	Mercuric Lead Bismuth Cupric Cadmium Arsenic Antimony Tin	HgS, black PbS, black Bi <sub>2</sub> S <sub>3</sub> , black CuS, black CdS, yellow As <sub>3</sub> S <sub>3</sub> , As <sub>2</sub> S <sub>5</sub> , yellow Sb <sub>2</sub> S <sub>3</sub> , Sb <sub>2</sub> S <sub>5</sub> , orange SnS, brown SnS <sub>2</sub> , yellow	The filtrate from group I is treated with hydrogen sulphide after adjusting the acidity to 0.3 normal.
III	Iron Chromium Aluminium	Fe(OH) <sub>3</sub> , red-brown Cr(OH) <sub>3</sub> , green Al(OH) <sub>3</sub> , white	Boil the filtrate from group II to remove H <sub>2</sub> S ; oxidize iron to ferric ion ; and add ammonium hydroxide.
IV	Cobalt Nickel Manganese Zinc	CoS, black NiS, black MnS, pink ZnS, white	To the filtrate from group III add ammonium sulphide.
V	Barium Strontium Calcium	BaCO <sub>3</sub> , white SrCO <sub>3</sub> , white CaCO <sub>3</sub> , white	Remove sulphides and excess ammonium ions by evaporation and dry heating ; and add ammonium carbonate.
VI	Magnesium Sodium Potassium Ammonium		Individual tests for each in the properly prepared filtrate from group V. Ammonium test made on original unknown.

**Group III :** Silver nitrate produces a white precipitate soluble in nitric acid, and barium chloride also produces a precipitate soluble in nitric acid : sulphites, selenites, tellurites, phosphites, carbonates, oxalates, iodates, borates, molybdates, tartrates, citrates, metaphosphates, and pyrophosphates.

**Group IV :** Silver nitrate forms a coloured precipitate soluble in nitric acid, and barium chloride also produces a precipitate soluble in nitric acid : orthophosphates, arsenates, arsenites, vanadates, thio-sulphates, chromates, and periodates.

**Group V :** Neither silver nitrate nor barium chloride produces a precipitate : nitrate, chlorate, perchlorate, persulphate, permanganate.

**Group VI :** Silver nitrate produces no precipitate, and barium chloride produces a precipitate insoluble in nitric acid : sulphates, fluorides, fluosilicates.

**Group VII :** Non-volatile acids which form precipitates with both silver nitrate and barium chloride, and both precipitates are insoluble in nitric acid : silicates, tungstates and anions of some rare elements.

After identifying the group into which the anion falls confirmatory tests must be made for the individual acid ions.

**References :** *Fresenius' Qualitative Analysis* (J. and A. Churchill, London) ; *A Manual of Chemical Analysis : Qualitative and Quantitative*, by G. S. Newth (Longmans, Green and Co., London) ; *Prescott and Johnson's Qualitative Chemical Analysis*, by R. K. McAlpine and B. A. Soule (D. Van Nostrand Co., New York) ; *A System of Qualitative Analysis of the Elements*, by A. A. Noyes (Macmillan and Co., London and New York) ; *Qualitative Analysis*, by A. A. Noyes and E. H. Swift (Macmillan and Co., London and New York) ; *Analytical Chemistry*, Vol. 1, *Qualitative Analysis*, by F. P. Treadwell, translated by W. T. Hall (John Wiley and Sons, New York) ; *Organic Chemistry*, and *Reagents*.

**QUANTITATIVE ANALYSIS** (see also *Analytical Chemistry*) — That part of analytical chemistry dealing with the ways and means of determining the exact amount of each constituent present in a substance. The general operations of quantitative analysis are as follows :

- I. Sampling.
- II. Preliminary examination.
- III. Qualitative analysis.
- IV. Drying of sample.
- V. Weighing.
- VI. Solution of sample.
- VII. Analysis by one or more of the following methods :
  - A. Gravimetric analysis :
    - (1) Preliminary treatment and purification.
    - (2) Precipitation.
    - (3) Filtration and washing.
    - (4) Drying and final heat treatment.
    - (5) Cooling and weighing.
    - (6) Calculation of per cent. purity.

## B. Volumetric analysis :

- (1) Preliminary treatment and purification.
- (2) Titration.
- (3) Calculation of per cent. purity.

## C. Gas analysis.

## D. Physico-chemical methods :

## (1) Mechanical :

- (a) Specific gravity.

## (2) Thermal :

- (a) Transition points.
- (b) Heat conduction.

## (3) Electrical :

- (a) Conductance.
- (b) Decomposition voltage.
- (c) Dielectric constant.
- (d) Magnetic susceptibility.

## (4) Optical :

- (a) Emission spectra.
- (b) Absorption spectra :
  - (i) Colorimetry.
  - (ii) Spectrophotometry.
- (c) X-ray diffraction.
- (d) Nephelometry.
- (e) Refraction :
  - (i) Index of refraction.
  - (ii) Interferometry.
- (f) Optical rotation.

## (5) Sonic effects.

*References :* *Fresenius' Quantitative Analysis* (J. and A. Churchill, London); *Analytical Chemistry*, Vol. 2, *Quantitative Analysis*, by F. P. Treadwell, translated by W. T. Hall (John Wiley and Sons, New York); *Standard Methods of Chemical Analysis*, by W. W. Scott (D. Van Nostrand Co., New York); *Quantitative Chemical Analysis*, by Clowes and Coleman; *Technical Methods of Analysis*, by R. C. Griffin (McGraw-Hill Book Co., New York); *Applied Inorganic Analysis* (special reference to metals, minerals, and rocks), by W. F. Hillebrand and G. E. F. Lundell (John Wiley and Sons, New York); *Analytical Methods for Certain Elements* (including cerium, thorium, molybdenum, tungsten, radium, uranium, vanadium, titanium, and zirconium), by R. B. Noore *et al.*, U.S. Bureau of Mines Bull., 122 (Superintendent of Documents, Washington, D.C.); *Quantitative Analysis*, by W. C. Pierce and E. L. Haenisch (John Wiley and Sons, New York); "The Chemical Analysis of Things as They Are," by G. E. F. Lundell (*Ind. Eng. Chem., Anal. Edit.*, 5, July 15 (1933)); Organic Analyses, and Volumetric Analyses.

**QUANTUM THEORY** — In 1900 Max Planck developed a line of reasoning to explain "black-body" radiation that has been expanded into what is called the Quantum Theory. There are two main ideas in

quantum theory : first, that radiation of energy is discontinuous, that is to say, it is in multiples of basic units or packets called quanta ; and, second, there are restrictions imposed in transferring energy to molecules and electrons. According to this theory the amount of energy ( $e$ ) associated with a given quantum is proportional to the frequency of the radiation ( $\nu$ ) by the equation  $e=h\nu$ , where  $h$  is Planck's constant and has the value of  $6.624 \times 10^{-27}$  erg-second.

While the Quantum Theory explains many things about light and the structure of atoms, it does not explain certain phenomena, such as diffraction of radiation and the fine structure of atomic spectra. The new quantum theory or *wave mechanics* attempts to correlate these phenomena with the ideas of Planck and Einstein. One of these systems was worked out by Heisenberg in 1925 and involved pure mathematics based upon his "uncertainty principle," which says in effect that for a small particle moving with a velocity approaching the velocity of light it would be impossible to state both its position and velocity simultaneously. Another of the wave mechanics systems was developed by Schrödinger in 1926 based upon the suggestion of L. de Broglie in 1924 that every particle is associated with a wave, and the wave length ( $\lambda$ ) is related to the mechanical momentum ( $mv$ ) by the relation  $\lambda=h/mv$ . The new wave mechanics has been helpful in treating experimental data and in developing the energy concept of the atom.

*References* : "Chemistry and the Quantum Theory," by Niels Bohr (*J.C.S.*, 1932, 349) ; *Quantum Chemistry*, by A. Haas (Constable and Co., London) ; *Quantum Theory*, by W. C. McC. Lewis (Longmans, Green and Co., New York and London) ; Southern's *Electricity and the Structure of Matter* (Oxford Univ. Press) ; Codd's translations of *Wave Mechanics and the New Quantum Theory*, by A. Haas (Constable and Co., London) ; *The Principles of Quantum Mechanics*, by P. A. M. Dirac (Oxford Univ. Press : Humphrey Milford, London) ; *Quantum Theory*, by F. A. Lindemann (Clarendon Press, Oxford) ; *Atomic Theory and the Description of Nature*, by N. Bohr ; *Textbook of Physical Chemistry*, by Glasstone (D. Van Nostrand Company, New York) ; *Atomic Spectra and Atomic Structure*, by Herzberg (Prentice-Hall, New York) ; *Introduction to Quantum Mechanics*, by Pauling and Wilson (McGraw-Hill Book Co., New York) ; *Introduction to Modern Physics*, by Richtmeyer and Kennard (McGraw-Hill Book Co., New York) ; Bohr's Theory, and Photon.)

**QUARTZ** — Anhydrous crystalline forms of silica sometimes met with chemically pure (crystal system No. 3, and sp. gr. 2.5 to 2.8). Rock crystal is a variety of water-white character, used in making lenses for spectacles ; other varieties are tinted, yellow ones being known as "false topaz," whilst amethyst is purple or violet. "Common quartz" occurs also in many varieties, some of which are opaque ; others more or less transparent, "milk quartz" being somewhat opalescent, and "cat's-eye" in yellow and green forms. The compact type of quartz includes the green chrysoprase (a kind of hornstone) and jasper of

several shades (brown, yellow, and red) containing iron. The chalcidies are also members of the quartz family of minerals, being mixtures of crystalline and amorphous silica, including cornelian, agate, and onyx.

Fused quartz obtained by electric heating is now used to make vessels which resist sudden heating and the action of acids, being employed among other applications for the concentration of sulphuric acid. Quartz is stable at all temperatures below  $870^{\circ}\text{C}$ . Many samples of fused quartz show phosphorescence when heated after being illuminated by ultra-violet light. (See Glass, Kieselguhr, Opal, and Silicon.)

**QUASSIA (Quassia Wood)** — The dried stem-wood of *Picræna excelsa* (Fam. Simarubaceæ), a tree growing in Jamaica and the West Indies. It contains two bitter principles,  $\alpha$ -picrasmin and  $\beta$ -picrasmin; aqueous infusions of quassia are used in medicine as bitters. Surinam quassia, from *Quassia amara*, contains about 0.03 per cent. of a bitter principle, quassiin ( $\text{C}_{10}\text{H}_{12}\text{O}_3$ ). (See Insecticides.)

**QUEBRACHO** — The dried bark of *Aspidosperma Quebracho* (Fam. Apocynaceæ), an evergreen tree growing abundantly in the rich Chaco forests of Bolivia, Brazil, and the River Plate districts of Argentine and Paraguay. An extract of quebracho is used in tanning and dyeing as a substitute for catechu and sumach.

Three varieties of quebracho are known, namely, "Colorado" or red, "blanco" or white, and "inale" or strong quebracho. White quebracho contains the alkaloids aspidospermine, yohimbine, and quebrachamine. Colorado quebracho is the most important variety commercially, being one of the main sources of the tannin extract of commerce. The dry extract contains about 65 per cent. of tannin and is prepared from the heartwood of the tree, the sapwood and bark which contain less tannin being neglected. In addition to untreated extracts, sulphited extracts prepared by Renner's process have been marketed under the designations "Crown," "Bestanino," etc. (See Yohimbine.)

**QUERCETIN (Meletin, Flavin)** ( $\text{C}_{15}\text{H}_{10}\text{O}_7 \cdot \text{H}_2\text{O}$ ) — A yellow crystalline substance, m.p.  $313^{\circ}\text{C}$ .; soluble in alkaline solutions, practically insoluble in water. It is prepared from quercitrin. Present in the rinds of various fruits, and in the leaves of *Magnolia Yulan* (B.C.A., A, 1931, 131). (See Allan and Robinson (*J. Chem. Soc.*, 1926, 2334); "The Position of the Sugar Nucleus in the Quercetin Glucoside," by Atree and Perkin (*J. Chem. Soc.*, 1927, 238); and Quercitrin.)

**QUERCITOL (Pentahydroxycyclohexane)** ( $\text{C}_6\text{H}_7(\text{OH})_5$ ), or so-called acorn-sugar, is a colourless, crystalline, sweet substance extracted from acorns. It is soluble in water, optically active and melts at  $235^{\circ}\text{C}$ .

**QUERCITRIN** ( $\text{C}_{21}\text{H}_{22}\text{O}_{12} \cdot 2\text{H}_2\text{O}$ ) — A yellow crystalline dyestuff (flavonol) of glycoside character extracted by alcohol from the bark of the *Quercus tinctoria*, also known as dyer's oak (a native of North America), which yields quercetin ( $\text{C}_{15}\text{H}_{10}\text{O}_7$ ) and rhamnose ( $\text{C}_6\text{H}_{12}\text{O}_5$ ) upon hydrolysis. Quercitrin has also been found present in the fresh leaves of *Camellia theifera* and in dried tea (to the extent of about 0.1 per cent.).

**QUERCITRON** — The powdered bark of *Quercus tinctoria*, the extract of which contains quercitrin, together with other substances; used in tanning and in dyeing textiles.

**QUICKLIME** — See Calcium (Oxide).

**QUICKSILVER** — Mercury (see same).

**QUILLAIA (Quillaya, Soap Bark, Panama Bark)** — The dried inner part of the bark of *Quillaja saponaria*, a tree growing in Bolivia, Peru, and Chile. It contains two toxic glycosides, quillaic acid and quillaia-sapotoxin, which are classified as saponins. Extracts of quillaia have the property of reducing surface tension and are used as foaming-agents, for shampooing, and as emulsifiers. (See Saponins.)

**QUILLAIC ACID** — See Saponins.

**QUINHYDRONE** ( $C_6H_4O_2 + C_6H_4(OH)_2$ ) is a green crystalline, additive substance—the addition product of quinone and hydroquinone. Used in making determinations of hydrogen-ion concentration. (See *pH* Value, and Hydrogen-Ion.)


**QUINIC ACID** ( $(HO)_4C_6H_7COOH$ ) — A white crystalline substance found in coffee beans, quinine bark, the common holly, the leaves of some conifers, and the cedar; soluble in water and alcohol; m.p. 163° C.

**QUINIDINE** — See Cinchona.

**QUININE** — See Cinchona.

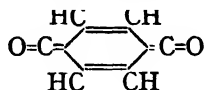
**QUINIZARINE (1, 4-Dihydroxyanthraquinone)** ( $C_6H_4(CO)_2C_6H_2(OH)_2$ ) — An orange red crystalline substance, m.p. 200–202° C., soluble in alcohol and ether, used in production of green and other dyestuffs. Related structurally to alizarin, which is the corresponding 1, 2 compound.

**QUINOL** — See Hydroquinone.

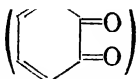
**QUINOLINE** ( $C_9H_7N$ ; ) — A colourless, highly refractive liquid of peculiar characteristic odour, present in coal tar and bone oil, and produced synthetically among other methods from aniline. It can also be made from cinchonine. Its b.p. is 238° C. and sp. gr. 1.095, and it is soluble in water and alcohol; used in medicine and for preserving anatomical specimens. (See Morton, *The Chemistry of Heterocyclic Compounds* (McGraw-Hill Book Co., New York).)

**QUINONES** — A group of yellow compounds used in dyestuffs, obtained from benzene and its derivatives by methods which replace 2 atoms of hydrogen by 2 of oxygen, for example, quinone (benzoquinone) ( $C_6H_4O_2$  or  $CO(CH_3)_2CO$ ), which is prepared from a solution of quinol by the addition of chromic acid, and also made by an oxidation process from aniline. It crystallizes in yellow needles, is soluble in alcohol and ether, melts at 116° C., and forms both monoxime and dioxime with hydroxylamine.

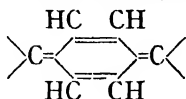
The quinoid formula illustrates the constitution of *1*, *4*- or *para*-benzoquinone, and exhibits the characteristic arrangement of double



Toluquinone ( $\text{CH}_3 \cdot \text{C}_6\text{H}_3\text{O}_2$ ) and naphthoquinone ( $\text{C}_{10}\text{H}_6\text{O}_2$ ), in common with benzoquinone, are used in so-called quinone tannage.

Ortho-benzoquinone () is a *red*, odourless, and non-volatile solid, decomposing at  $60^\circ$  to  $70^\circ$  C. (See Anthraquinone.)

**QUINONOID STRUCTURE** — The chromophoric grouping



in certain compounds that exist in coloured and colourless forms, such as phenolphthaleïn and *para*-nitrophenol, is believed to be responsible for the development of colour, the colourless form being obtained under conditions that do not favour the formation of the quinonoid structure.

**QUINOPHAN** — See Cinchophen.

**" QUINOXYL "** — See Chiniofon.

**QUINTESSENCES** — See Perfumes.

**R** — An abbreviation for any monovalent radical.  $\text{R}^1$  is sometimes used to distinguish aryl (for example, phenyl) from alkyl (R) (for example, methyl.)

**R SALT** — An intermediate, being the sodium salt of beta-naphthol-3, 6-disulphonic acid. (See Acid R.)

**RACEMATES** — Salts of racemic acids.

**RACEMIC ACID** ( $(\text{C}_4\text{H}_6\text{O}_6)_2 \cdot 2\text{H}_2\text{O}$ ) — A transparent crystalline form of tartaric acid ( $\text{C}_4\text{H}_6\text{O}_6$ ) obtained from tartar mother-liquor, devoid of the power of turning the plane of polarized light, and therefore termed "inactive," but by external compensation, since it admits of division into two modifications having equal but opposite rotatory powers: the one known as dextro-tartaric acid, which turns the polarized light plane to the right; and the other as lævo-tartaric, which turns it to the left. It is soluble in water, and melts at  $205^\circ$  C. Its salts are termed racemates and exhibit differences from the tartrates in solubility, melting-points, and other respects. (See Tartaric Acid.)

**RACEMIC COMPOUNDS** are mixtures of equal parts of the dextro and lævo modifications (isomers) of compounds, and are, in consequence, optically inactive by external compensation, for example, racemic acid. When sodium ammonium racemate ( $\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ ) is crystallized from a concentrated hot solution the crystals are all of exactly the same form—each individual crystal consists of equal parts of dextro and lævo forms and is optically inactive. But crystallization below the critical temperature (transition point) of  $28^\circ \text{C}$ . produces two different sets of crystals that are equal in amount but one set dextro and the other set lævo in optical activity, namely, sodium ammonium *d*-tartrate and sodium ammonium *l*-tartrate side by side (both of formula  $\text{Na}(\text{NH}_4)\text{C}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ ). Thus crystallization below the critical temperature furnishes two distinct “hemihedral” forms, which are not superimposable and are to each other as object and mirror image, but in all respects *save in their opposite optical activities* are identical—same melting point, same solubility in solvents, same density, and identical in chemical reactivity. This phenomenon was discovered by Louis Pasteur in 1848, and only a few other examples have been found since then wherein the crystals have been large enough to be separated by hand picking using a lens as he did. The explanation for this remarkable phenomenon was proposed separately and practically simultaneously by van 't Hoff (September, 1874) and Le Bel (November, 1874) that these are isomers in space. Racemic compounds in solution are identical with the corresponding racemic mixtures, but in the crystalline form they differ as described. (See Isomerism, and Stereoisomerism.)

**RACEMIZATION** — The process of converting an optically active substance into the corresponding racemic mixture. The degree of ease with which this may be accomplished varies greatly from one compound to another; for instance, *l*-hyoscyamine may readily be converted to atropine, the *dl*-form, merely by heating with very dilute alkali, and some substances are so readily racemized that the separation of the optical enantiomorphs is well-nigh impossible; such substances very readily revert to the racemic form in the presence of a trace of impurity.

**RADIANT ENERGY** — Light, radiant heat, and electrical waves. The mechanical effects of radiant energy are shown and measured by an instrument termed a “radiometer,” and minute changes of radiant energy are detected by the radiomicrometer (a sensitive thermopile). (See Energy, Light (Photochemical Aspects), Photons, Photocatalysis, Radioactivity, and Wave Lengths.)

**RADICALS** — Groups of atoms which behave in replacement value in chemical combinations as atoms, for example, the group  $\text{CH}_2$  in the homologous “paraffin” series of hydrocarbons; the group  $\text{OH}$  in the alcohols; the group  $\text{C}_3\text{H}_5$  (glyceryl) in fats; the group  $\text{NO}_2$  in nitric acid and many explosives; and the group  $\text{SO}_4$  in sulphuric acid. Radicals may be mono-, di-, or trivalent, etc., that is to say, capable of replacing one, two, three or more monovalent atoms.

**Free radicals** of both the aromatic and the paraffin series are known. Isolated by Gomberg in 1900 the first recognized organic free radical was triphenylmethyl obtained by the action of silver on triphenylchloromethane. In the solid state triphenylmethyl as colourless crystals shows remarkable stability, having been reported by Gomberg to be as active after twenty years as when first made. In solution it has been found that these are coloured yellow, and the solution consists of an equilibrium mixture of mono- and dimolecular modifications. Dilution with solvent displaces the equilibrium in the direction of producing more of the monomolecular form and a deepening of colour, whereas removal of solvent displaces the equilibrium in the opposite direction until in concentrated solutions the colour almost disappears.

Free methyl radicals were demonstrated by Paneth in 1929 by heating lead tetramethyl at low pressure in a stream of hydrogen. The half-life of the methyl radical is about 0.006 second. The free radical is allowed to impinge on a metallic mirror, which is seen to distil away. Under the influence of the free radical a volatile organo-metallic compound is formed. Free radicals are of interest in connection with the kinetics of organic reactions (Studied by Rice). (See F. O. Rice and O. L. Polly on "Formation of Alicyclic Hydrocarbons from Free Radicals" (*Ind. Eng. Chem.*, **27**, 915 (1935)) ; *Ann. Rep. Prog. Chem.*, **34**, 264 (1937) ; **42**, 87 (1946).)

**RADIOACTIVITY** is a phenomenon exhibited by certain of the chemical elements of high atomic number and atomic weight, principally uranium (At. No. 92) and thorium (At. No. 90), and their break-down products, for example, radium (At. No. 88) from uranium. The phenomenon was originally discovered by Becquerel in 1896 through the effect produced on a photographic plate in the dark by a specimen of pitchblende placed near the plate. Pitchblende contains the element uranium, and it was later shown that uranium both in natural and in artificial substances possesses the same property. This discovery was followed by that of M. and Mme Curie, that the activity of the uranium compounds is in part due to the presence in them of some other very active substance, namely, radium, which proved to be a million times more active than uranium.

Other properties, besides that of causing a change in a photographic plate in the dark, were discovered, for example, the discharge of a charged electroscope, phosphorescence in the dark, and the evolution of sufficient heat to maintain a temperature higher than that of the surroundings.

A study of all radioactive substances has shown that **three types of radiation** are emitted, and these have been named alpha, beta, and gamma. These three radiations resemble anode rays, cathode rays, and X-rays, respectively.

Alpha rays consist of helium nuclei shot off from the interior of atoms of certain elements, and possess a definite velocity and a definite range for each element. The velocity is from 5 to 7 per cent. of that of light. The range is the distance travelled in a homogeneous medium before absorption. Geiger and Nuttall in 1911 showed that the range

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is proportional to the cube of the velocity. The penetrating power of alpha rays is the lowest of the three types of radiation. Their relative penetrating powers are approximately 1 for alpha, 100 for beta, and 10,000 for gamma. Alpha rays are particles of helium carrying two unit positive charges, thus  $\text{He}^{++}$ , and when the double positive charge is lost (or two electrons gained) the product is ordinary helium. When a chemical element loses an alpha particle from its atom, the residual element is 4 units of atomic weight (or proton number) less than the original element (atomic weight of helium is 4), and 2 units of positive valence less than the original element, thus radium of atomic weight 226 and showing valence of +2 in compounds, as does barium, loses an alpha particle and becomes radon of atomic weight 222 and exhibits a valence of 0, as does argon. The detection and counting of *single* alpha particles can be accomplished by the use of the electrometer or the spinthariscopes.

Beta rays consist of electrons ( $e^-$ ) that are shot off from the interior of radioactive atoms with velocities varying almost up to that of light. The beta radiation is highly deflected in an electrical or a magnetic field, as are cathode rays. When a chemical element loses a beta particle from its atom, the residual element is of the same atomic weight (or proton number) (atomic weight of the electron is only  $1/1800$  part of that of hydrogen), and 1 unit of negative valence less than the original element, thus, mesothorium-1 of atomic weight 228 and showing a valence of +2 in compounds, as does barium, loses a beta particle and becomes mesothorium-2 of atomic weight 228 and exhibits a valence of +3, as does aluminium.

Gamma rays are like X-rays, except that they are more penetrating than the latter; so penetrating are they, in fact, that Rutherford states that the presence of gamma rays from 30 milligrams of radium can be detected by the electroscope after passage through 30 centimetres (11.75 inches) of iron. By diffraction through crystals, the wave length of gamma rays has been determined to be from about  $10^{-8}$  centimetre for the soft gamma rays of the element radium B to about  $0.7 \times 10^{-9}$  centimetre for the hard gamma rays of the element radium C.

**End Products** — The end product of the uranium-radium series indicates lead of atomic weight 206.0 (atomic weight of ordinary lead 207.21), the end product of the thorium series indicates lead of atomic weight 208.0, and the end point of the actinium series, which is a branch of the uranium series, indicates lead of atomic weight 207.0. T. W. Richards, in 1916, determined the atomic weight of lead in certain radioactive minerals as follows: Joachimsthal pitchblende 206.57, Colorado carnotite 206.59, and North Carolina uranite 206.40.

**Artificial Disintegration of the Elements** — This has been known since Rutherford in 1919 disintegrated the nitrogen atom by bombardment with alpha particles fired from Radium C (see Nuclear Chemistry).

**Artificial Radioactivity** — Numerous projectiles have been used in atomic bombardment since the original work of Rutherford in 1919. There have been used as such (1) alpha particles, of mass 4, positive

charge 2, helium; (2) protons, of mass 1, positive charge 1, hydrogen; (3) neutrons, of mass 1, charge 0, hydrogen; and (4) deuterons, of mass 2, positive charge 1, deuterium (isotope of hydrogen having mass 2, whereas ordinary hydrogen is of mass 1). In 1934, M. and Mme F. Joliot, working at the Curie Institute of Radium, Paris, produced artificially radioactive substances by the bombardment with alpha particles of aluminium, boron, and magnesium, and E. O. Lawrence, working at the University of California, Berkeley, produced radioactive sodium by bombardment of sodium with deuterons. The half-life of radiosodium is 15 hours.

There are many more artificial radioactive substances known than natural ones.

(See *A Manual of Radio-Activity*, by Hevesy and Paneth (Oxford University Press); *Radio Elements and Isotopes, etc.*, by K. Fajans (McGraw-Hill Publishing Co., New York); a chart of the Transformations of Radioactive Elements, and a table of the Constants of Radioactive Elements in the article on "Radioactive Changes" in *Van Nostrand's Scientific Encyclopedia* (D. Van Nostrand Co., New York); Atoms, Light, Photons, Radium, Transmutation, Wave Lengths, X-Rays, and especially Nuclear Chemistry.)

**RADIUM (Ra) and its Compounds** — Atomic weight, 226.05. See Elements for other data. Radium is a very rare, bright, white metal, the chief sources of which are *carnotite* and *pitchblende*, minerals found in Cornwall, Colorado, Turkestan, Madagascar, Utah, Belgian Congo, Olary in South Australia, North-Western Canada, Czecho-Slovakia, and elsewhere. Radium also occurs in *autonite*, a hydrated calcium uranium phosphate found in Portugal, and in *torbernite*, a hydrated copper uranium phosphate.

It has remarkable properties, and is an atomic decomposition product of the metal uranium, resembling barium in its chemical properties, and yielding crystalline salts, which are luminous in the dark, radioactive, and emit heat continuously so that they are thus able to maintain a temperature higher than that of their surroundings.

The radium family includes uranium, ionium, radium, radon, and polonium, all of which are severally referred to in this work.

The radiations of radium are used as a curative agency in medical practice, and its rays are very destructive of animal tissues. In emitting these radiations it is regarded as undergoing spontaneous decomposition, giving out heat continually, and yielding a succession of radioactive disintegration products, including radon, radio-lead (see Lead), and helium. (See Atoms, Elements, Nuclear Chemistry, and Radioactivity.)

The radium atom of atomic weight 226 loses a helium atom of atomic weight 4, and leaves a radon atom of atomic weight 222. It has been calculated that radium disintegrates at such rate that the time required for one-half of any given quantity to break up into other elements is 1600 years, and that the heat development of 1 milligram of radium is 0.132 calorie per hour.

The penetrating radium rays are capable of bringing about many chemical changes, among which may be instanced their action on toluene, resulting in the production of benzaldehyde and benzoic acid.

The **chloride** ( $\text{RaCl}_2$ ) is a soluble, yellowish-white, crystalline salt, which, mixed with calcium sulphide or the native zinc sulphide, *wurtzite*, is used in making luminous paints; whilst the **bromide** ( $\text{RaBr}_2$ ) (in which form radium is marketed) is a white crystalline salt similarly employed, and both are used in medicine (chiefly in the treatment of cancer). The **hydroxide** ( $\text{Ra}(\text{OH})_2$ ) is more soluble in water than barium hydroxide and these may be fractionally separated by crystallization.

**RADON** (Niton) (Rn) — Atomic weight, 222. See Elements for other data. A rare inert substance described as radium emanation, soluble in water, and prepared by heating a radium compound or by dissolving it in water, pumping off the gases slowly generated from it, then removing any associated oxygen, hydrogen, carbon dioxide, and nitrogen, thus leaving radon. It can be condensed to the liquid or solid state, and both forms are phosphorescent. It spontaneously decomposes into helium and a solid radioactive substance. (See Radioactivity.)

**RAFFIA** — See Raphia.

**RAFFINOSE** (Melitriose) ( $\text{C}_{18}\text{H}_{32}\text{O}_{16}, 5\text{H}_2\text{O}$ ) — A soluble trisaccharide, resembling cane sugar, but tasteless, occurring in sugar-beet and its molasses, and obtainable from cotton-seed meal and other sources. It is dextro-rotatory and on hydrolysis yields an equimolecular mixture of galactose, fructose, and glucose.

**RAGSTONE** — An impure limestone.

**RAISIN-SEED OIL** — See Grape-seed Oil.

**RAMAN EFFECT** — Results from a collision between a photon (light quantum) and a molecule under conditions that allow an interchange of some of the energy of the photon and the molecule. Part of the energy of the photon goes to displacing the atoms of the molecule, after which the molecule emits radiation and becomes deactivated, but not necessarily to the same energy state that it possessed before it was activated by the photon. After such a collision the scattered radiation has a different frequency from that of the incident radiation, and there is a change in the energy of atomic oscillation within the molecule.

The collision of a photon with a molecule may be represented by the relation: Energy of incident radiation *minus* the energy of the scattered radiation = change in molecular energy = energy of the Raman radiation. Since the energy of radiation ( $e$ ) is controlled by Planck's relationship  $e = h\nu$ , where  $h$  is Planck's constant and  $\nu$  is the frequency of the radiation, it follows that:

$$h\nu_{\text{incident}} - h\nu_{\text{scattered}} = h\nu_{\text{Raman}}$$

The difference in wave number (wave number =  $1/\text{wave length}$ ) between the incident and the scattered light permits a direct calculation

of the Raman shift, which is of the order of 100 to 4,000  $\text{cm}^{-1}$ . Usually, the frequency of the scattered light is less than that of the incident light, indicating that a quantum of radiation has given up part of its energy to produce interatomic motion within the molecule. It is possible in some cases for the incident radiation to absorb energy from the molecules and leave with greater energy.

Raman spectra are useful in the study of molecular structure, and various types of bonds are identifiable in complex organic and inorganic molecules.

*References:* "The Raman Effect," by Glocker (*Rev. Mod. Phys.*, **15**, 112 (1943)); *The Raman Effect and Its Chemical Applications*, by J. H. Hibben (Reinhold Publishing Corp., New York); *Scattering of Light and Raman Effect*, by S. Bhagavantam (Chemical Publishing Co., Brooklyn, New York); Raman Spectra, in *Ind. Eng. Chem., Anal. Ed.*, Oct., 1947; J. Newton Friend's *Textbook of Physical Chemistry* (Charles Griffin and Co., London; J. B. Lippincott Co., Philadelphia); and *Annual Reports of the Progress of Chemistry* (Chemical Society).

**RAMIE** (Rhea Ramie, or Chinese Grass) — The fibre of several varieties of the genus *Bæhmeria* (N.O. Urticaceæ), or the Rhea of Assam, now grown in India and Italy, and said to be nearly three times stronger than Russian hemp. It is obtained by the decortication and degumming of the white-leaved *Bæhmeria nivea* and the green-leaved *B. tenacissima*. The decorticated fibre yields 5.63 per cent. ash, contains 10.15 per cent. water, and yields a water extract of 10.34 per cent. It contains 0.59 per cent. fat and wax, about 66 per cent. cellulose, and 12.70 per cent. pectin bodies, while the degummed product, which is obtained by digestion of the last fibres in water, is practically pure cellulose, identical in composition with bleached cotton and linen, and can be dyed in common. It is used in China for making mats and sails; in Saxony for making tapestry, tablecloths, damasks, etc.; and is the principal yarn from which gas-mantle fabrics are knitted and woven. It is used in paper, rope, and cork making, also in the textile industry, and silk decoration.

**RANCIDITY** — See Fats.

**RAOULT-DALTON EQUATION** — In the calculation of vapour-liquid equilibria, Raoult's and Dalton's laws are usually combined in the form:  $p_a = \pi y_a = P_a x_a$ , where  $p_a$  = partial pressure of component  $a$  in the mixture,  $\pi$  = total pressure of the system,  $P_a$  = vapour pressure of the pure component at the temperature of the system,  $x_a$ ,  $y_a$  = mole fractions of component  $a$  in the liquid and vapour phases respectively. At high pressures the equation breaks down owing to deviations from Raoult's law and the ideal gas laws. By the substitution of fugacities for pressures, a similar relation is obtained which is more accurate at high pressures. (See Fugacity.)

**RAOULT'S LAW** — See Freezing Points.

**RAPE-SEED OIL (Colza Oil)** — A dark, non-drying, yellowish, fatty oil of unpleasant odour extracted by pressure from rape-seed, a plant of the cabbage tribe of the genus *Brassica* (*Brassica napus*, *campestris*, etc., N.O. Cruciferae). The best rape-seed comes from Shanghai and Hankow in a number of varieties, and a considerable quantity is raised in India, China, and Japan. It yields from 33 to 45 per cent. of oil, soluble in alcohol, carbon disulphide, ether, and chloroform; of solidifying point,  $-2^{\circ}$  to  $-10^{\circ}$  C., sp. gr., 0.9132 to 0.9168; sap. v., 170 to 179; ref. ind., 1.4725; and i.v., 94 to 104. It contains about 33 per cent. linolein, 10 per cent. saturated glycerides, the remainder being erucic and rapinic acids (about 44 per cent.). It can be "blown" like linseed oil, and is used to some extent for illuminating purposes, but chiefly for oiling woollen stuffs, and as a lubricant. The pressed cake is of value as a feeding stuff. It has been reported that a liquid of the same nature as petrol is obtained by the dehydrating action of molten zinc chloride upon rape-seed oil at  $350^{\circ}$  to  $400^{\circ}$  C.

In World War II rape-seed oil was extensively used as a substitute for olive oil in liniments and other preparations for external application, when the use of olive and arachis oils for this purpose was illegal. Its unpleasant odour is the main objection to its use in medicine.

**RAPHIA** — A fibre obtained by stripping the bast from the leaf of the palms that give piassava; it can be dyed like straw and is used in making mats and basket ware and for tying up plants. (See Piassava.)

**RARE-EARTH ELEMENTS** — Elements no. 57 to 71, inclusive. (See Elements.)

*Reference:* *The Rare-Earth Elements and Their Compounds*, by D. M. Yost *et al.* (John Wiley and Sons, New York).

**RARE GASES** — Elements of Group O. (See Elements.)

**RASORITE** — An American mineral hydrated sodium borate found in the Kramer district near California.

**RAYON** — Name used for certain silk substitutes, but not inclusive of all varieties. It applies to viscose silk, but not to cellulose acetate and other synthetic fibres. (See "Economic and Technical Aspects of the Rayon Industry," by E. B. Bengel (*Ind. Eng. Chem.*, 28, 511 (1936)); "Cordura"; Silk Substitutes; and Viscose.)

**RAYS** — See Nuclear Chemistry, Radiation, Radioactivity, Wave Lengths, and X-Rays.

**REACTION CHAMBER** — See Catalytic Reactor.

**REACTIONS** — See Chemical Interactions, and Gas Reactions.

**REACTOR (Pile)** — The arrangement used to produce a chain reaction with uranium. The original reactor, or pile as it was then called, was tried out successfully on December 2, 1942, at the University of Chicago. It consisted of blocks of graphite interspersed with pieces of uranium

metal. Reactors are used at Hanford, Washington State, to produce plutonium from uranium. Only neutrons with very low speed produce fission, and an element of low atomic weight such as carbon is necessary to cause the high-speed neutrons to lose some of their energy and attain the required low speed. Materials that function as graphite above are called moderators.

Much heat is produced in the fission process. When plutonium is the desired product this heat is dissipated by air or water. For power production by this process it becomes necessary to permit reactors to operate at high temperature to generate steam for use in turbines to drive electric generators. Reactors become intensely radioactive during their operation and all work with and on them must be done by remote control behind thick absorbing walls.

**REAGENTS** — Solutions used for testing purposes—that is to say, bringing about chemical reactions—in qualitative analysis, comprising strong hydrochloric, nitric, and sulphuric acids; dilute solutions of the same acids (approximately 5-normal (see below)); and various salts containing about 5 per cent. of the respective substances, dissolved in water.

For use in the practice of volumetric analyses, solutions of known strength, or so-called "standard solutions," are employed, the quantities of the constituents bearing the same relation to each other as the numbers which express their chemical equivalents. When they are made of such strengths that a litre (1,000 ml.) contains equivalent weights in grams, for example, 36.5 grams of NaCl in 1,000 ml., or 49 grams of H<sub>2</sub>SO<sub>4</sub>, they are termed "**normal** standard solutions." Formula weight of a chemical divided by the valence gives the weight for 1,000 ml. of 1.0 normal solution. (See Concentration, Volumetric Analyses.)

**REALGAR** (As<sub>2</sub>S<sub>2</sub>) — See Arsenic.

**REAUMUR** — Heat (Temperature).

**RECTIFICATION** — Fractional distillation, especially as applied to alcohol, petroleum, and coal-tar distillates. (See Distillation.)

**RED ANTIMONY** — See Antimony, and Kermisite.

**RED LEAD (Minium)** — See Lead (Oxides).

**RED LIQUOR** — See Aluminium (Acetate).

**RED OIL** — See Oleic Acid.

**RED OXIDE** — See Iron (Oxides), Ochre, and Reddle.

**RED PRUSSIATE** — Potassium and sodium ferricyanides respectively.

**REDDLE (Ruddle)** — An earthy, ochreous ore of iron (ferric oxide) associated with clay, chalk, or other mineral matter, from hematite deposits found in some English counties and elsewhere, and used by farmers for making a red paste to mark sheep.

**REDONDA PHOSPHATES** — Natural phosphates of iron and aluminium found in the islands of Redonda and Alta Vela.

**REDRUTHITE**— Mineral copper sulphide ( $\text{Cu}_2\text{S}$ ), of crystal system No. 4, and sp. gr. 5.5.

**REDUCING AGENTS** — Substances are said to act as reducing agents, as when, for example, oxygen is removed in some degree from an oxide or certain ores by the agency of hydrogen or carbon, or by the use of hydrocarbons or that of producer gas at an appropriate temperature for similar processes. Red lead is reduced to metallic lead by strongly heating it with charcoal. Ferric chloride ( $\text{FeCl}_3$ ) can be easily reduced to the lower ferrous chloride ( $\text{FeCl}_2$ ) by zinc or aluminium metal. Reduction can be effected by the addition of hydrogen to an organic compound through the agency of sodium amalgam. Members of the sugar series can be reduced by the action of aluminum amalgam, and the manufacture of aniline is carried out by a reducing process. (See Oxidation-Reduction.)

**REFINING** — See Petroleum.

**REFLUX CONDENSER** — See Dephlegmate, Extraction, and Rectification.

**REFORMING** — See Hydroforming.

**REFRACTION** — The effect which is produced when a ray of light passes from one medium to another, making a body partially immersed in water, for example, look as if it were broken. (See Refractive Index.)

**REFRACTIVE INDEX** — The index of refraction for any substance is a ratio of the velocity of light in a vacuum to its velocity in the substance. The extent to which a beam of light is refracted as it passes from one substance to another depends on the relative number (concentration) of atoms in the two substances, on the kind of atoms, and on the arrangement of atoms within the molecules.

When a light beam passes from one substance into another the direction of the beam is changed or bent or refracted. The angle of incidence ( $i$ ) of the light is the angle which the oncoming beam makes with a line perpendicular to the surface which separates the two substances. The angle of refraction ( $r$ ) is the angle the diffracted beam travelling in the second substance makes with reference to a line perpendicular to the separating plane surface. The ratio of the sines of these two angles is in the same ratio as the velocities of the light in the two media, and the index of refraction ( $n$ ) is defined by the equation.

$$n = \frac{\text{velocity of light in substance 1}}{\text{velocity of light in substance 2}} = \frac{\sin i}{\sin r}.$$

In general the index of refraction of a substance varies with the wave length of the light and with the temperature.

The index of refraction is useful in identifying many materials (see Oils, and Essential Oils). The accompanying table gives the refractive index of some familiar materials.

TABLE SHOWING THE REFRACTIVE INDICES OF SELECTED MATERIALS

Using light of the sodium-D line

Substance	Refractive Index, $n_D$	Substance	Refractive Index $n_D$
Water .. ..	1.333	Apatite .. ..	1.63-1.65
Ice.. ..	1.309	Calcite .. ..	1.658
Air .. ..	1.0029	Corundum .. ..	1.768
Acetaldehyde .. ..	1.339	Diamond .. ..	2.42
Acetic acid .. ..	1.372	Dolomite .. ..	1.682
Acetone .. ..	1.359	Fluorite .. ..	1.434
Aniline .. ..	1.586	Garnet .. ..	1.7-1.9
Benzaldehyde .. ..	1.546	Gypsum .. ..	1.523
Benzene .. ..	1.501	Halite (rock salt) .. ..	1.544
Carbon disulphide .. ..	1.628	Magnesite .. ..	1.717
Carbon tetrachloride .. ..	1.463	Orthoclase .. ..	1.524
Chloroform .. ..	1.446	Quartz .. ..	1.544
Cyclohexane .. ..	1.426	Sulphur .. ..	2.038
Ether .. ..	1.350	Topaz .. ..	1.631
Ethyl acetate .. ..	1.373	Glass, crown .. ..	1.48-1.61
Ethyl alcohol .. ..	1.361	Glass, flint .. ..	1.53-1.96
Ethyl bromide .. ..	1.424	Plastics :	
Ethylene glycol .. ..	1.432	Cellulose acetate .. ..	1.50
Glycerol .. ..	1.473	Cellulose nitrate .. ..	1.50
n-Hexane .. ..	1.375	Urea-formaldehyde .. ..	1.60
Nitrobenzene .. ..	1.552		
Phenol .. ..	1.540		
Toluene .. ..	1.497		

**REFRACTOMETER** — An instrument for measuring the velocity of propagation of light in a substance, this velocity being inversely proportional to the refractive index of substances. The refractive index is constant for every pure substance under standardized conditions of temperature and pressure.

There are refractometers for various purposes, one of the best for purely scientific work being the "Pulfrich," used for investigating optical glasses, etc. The so-called "Butyro" and "Oleo" refractometers, such as the "Abbe Zeiss" and "Féry" instruments, are largely used for butter, oils, and fats; while other instruments are the "Abbe" (which is used for liquids and also utilized in the determination of melting-points), the "Jamin," the "Rayleigh," the "Bausch and Lomb," and the "Spencer."

**REFRACTORIES** are substances difficult to fuse, including materials employed in the construction of furnaces, ovens, kilns, retort settings, furnace hearths, stoves, crucibles, etc., affording resistance to heat, abrasion, strain, and the action of gases or other chemical compounds to which they are exposed in use.

	Type of Brick	Composition	P.C.E. or Fusion Point	True Specific Gravity	Approx. Weight in lb. of 9-in. Brick	Linear Coefficient of Expansion per ° C.
ACID	Silica	SiO <sub>2</sub> 95-96%	31-33 Cone	2.3-2.4	6	See (A) below)
	High Heat Duty Fire-brick	Al <sub>2</sub> O <sub>3</sub> 35-42% SiO <sub>2</sub> 52-60%	31-33 Cone	2.60-2.70	7½-8	53 × 10 <sup>-7</sup> 20°-1,200° C.
	Super Duty Fire-brick	Al <sub>2</sub> O <sub>3</sub> 43-44% SiO <sub>2</sub> 51-53%	33-34 Cone	2.65-2.75	7½-8	53 × 10 <sup>-7</sup> 20°-1,200° C.
	High Alumina Fire-brick	Al <sub>2</sub> O <sub>3</sub> 50-80%	34-39 Cone	2.80-3.40	8-9	53-65 × 10 <sup>-7</sup> 20°-1,425° C.
	Kaolin	Al <sub>2</sub> O <sub>3</sub> 44-45% SiO <sub>2</sub> 51-53%	31-34 Cone	2.60	7½-8	53 × 10 <sup>-7</sup> 20°-1,425° C.
	Mullite	Al <sub>2</sub> O <sub>3</sub> 62% SiO <sub>2</sub> 38%	38 Cone	3.03	8½	45 × 10 <sup>-7</sup> 20°-1,320° C.
	Zircon	ZrO <sub>2</sub> 67.1% SiO <sub>2</sub> 32.9%	Approx. 4,400° F.	4.6	12	42 × 10 <sup>-7</sup> 20°-1,550° C.
NEUTRAL	Silicon Carbide	SiC 89-91%	Dissoc. at 4,082° F.	3.13-3.22	9.5	45 × 10 <sup>-7</sup> 20°-1,100° C.
	Graphite	C 100%	Above 5,432° F.	2.25	8	20 × 10 <sup>-7</sup> 20°-1,000° C.
	Chrome	Cr <sub>2</sub> O <sub>3</sub> 30-45% Al <sub>2</sub> O <sub>3</sub> 15-33% SiO <sub>2</sub> 11-17% FeO 3-6%	3,550°-4,000° F.	3.8-4.1	11	80 × 10 <sup>-7</sup> 20°-1,000° C.
	Fused Alumina	Al <sub>2</sub> O <sub>3</sub> 90-99.1%	38-41 Cone	3.80-4.00	11	70 × 10 <sup>-7</sup> 20°-1,000° C.
BASIC	Forsterite	MgO 57.3% SiO <sub>2</sub> 42.7%	40 Cone	3.3-3.4	9	110 × 10 <sup>-7</sup> 20°-1,500° C.
	Magnesia-Alumina Spinel	MgO 28.2% Al <sub>2</sub> O <sub>3</sub> 71.8%	3,875° F.	3.6	10	80 × 10 <sup>-7</sup> 20°-800° C.
	Magnesite (Dead Burned)	MgO 83-93% Fe <sub>2</sub> O <sub>3</sub> 2-7%	3,992° F.	3.4-3.6	9½	147 × 10 <sup>-7</sup> 20°-1,425° C.
	Magnesia (Electrically fused)	MgO 94-96% SiO <sub>2</sub> 2-3% CaO 1-2%	3,992-4,532° F.	3.60	10	150 × 10 <sup>-7</sup> 20°-1,475° C.

\* To change B.Th. Units to C.G.S. Units divide by 2903.

(A) 430 × 10<sup>-7</sup>, 20°-300° C., 30 × 10<sup>-7</sup>,

Authority: W. H. Henson, *American Foundryman*, May, 1947.

## REFRACTORIES

Thermal Conductivity, B.Th.U./hr./sq. ft./in./° F.	Mean Specific Heat (cgs)	Deformation under Load 25lb./sq. in.	Constancy of Volume	Remarks
13.0 390°-1,832° F.	0.265 70°-1,832° F.	No deformation at 2,732° F., 50 p.s.i.	Low shrinkage. Rev.† exp. to melting point	Strongly resistant to acid slags. Readily attacked by basic materials and fluorides.
400°-2,400° F. 9.5	0.26 70°-1,830° F.	4.0 + % at 2,460° F.	2.0% shrink at 2,550° F.	Rapidly attacked by basic slags, particularly iron slags. Moderately resistant to acid slags.
Approx. same as High Heat Duty	Approx. same as High Heat Duty	2.5 to 4.0% at 2,460° F.	1% max. shrink. at 2,732° F.	
Slightly more than High Heat Duty	Approx. same as High Heat Duty	Approx. same as Super Duty	0-3% shrink. at 2,912° F.	More resistant to alkali slags than fire-clay brick; readily attacked by iron slags.
13.5 at 2,400° F.	0.254 480°-1,832° F.	1% at 2,800° F.	0.5% shrinkage at 3,000° F.	Slightly more resistant than fire-brick to slags, particularly basic slags.
8.5 200°-2,600° F.	0.175 70°-1,475° F.	0 at 2,650° F., 50 p.s.i. 2.0% at 3,000° F., 50 p.s.i.	No appreciable change to 3,000° F.	Low solubility in glasses and some slags. Attacked by high-iron slags.
13.5 390°-1,832° F.	0.132 100° F.	Fails at 2,820°- 2,910° F.	No appreciable change to 2,820° F.	Not readily attacked by acid slags. Readily attacked by basic slags and fluorides.
66.0 at 2,000° F.	0.186 70°-1,832° F.	No deformation to 2,732° F., 50 p.s.i.	No shrinkage to 2,732° F.	Readily attacked by strongly basic slags, particularly those high in iron or calcium oxides.
220 at 2,000° F.	0.29 70°-1,832° F.	None	No shrinkage	Strongly resistant to all slags except those containing oxides readily reduced.
12.1 at 2,400° F.	0.22 at 1,832° F.	No deformation at 2,600° F.	1.3% shrinkage at 2,820° F.	Neutral properties. Not readily attacked by acid or basic slags.
18.0-20.0 at 2,000° F.	0.174-0.304 32°-1,832° F.	1-2% at 2,732° F., 50 p.s.i.	No shrinkage at 2,732° F.	Very resistant to acid slags, moderately resistant to basic slags; tendency to absorb.
10.3 at 2,400° F.	0.22 70°-200° F.	No deformation to 2,730° F., 50 p.s.i.	Negligible shrinkage to 3,000° F.	Not readily attacked by basic slags; readily attacked by acid slags.
14.5 at 2,400° F.	0.25 70°-1,832° F.			Moderate resistance to basic slags; low resistance to acid slags. Magnesite spinel sometimes shows slag absorption.
13 2,400° F.	0.278 70°-1,832° F.	Poor load-bearing property above 2,450° F.	No shrinkage below 2,900° F.	Not readily attacked by basic slags; readily attacked by acid slags.
20.0 2,000° F.	0.292 32°-2,375° F.	Poor load-bearing property above 2,732° F.	Less than 1% below 3,250° F.	

300°-1,100° C.

† Reversible.

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Some refractories melting at about  $1,800^{\circ}\text{C}$ . are made by heating mixtures of kaolin and alumina, or bauxite and fire-clay.

Clays, fire-clays, and silica in the forms of flint, dinas rock, quartz, sandstone, and ganister are described as acid refractories, containing as they do silicic acid alone or in combination (as in the clays) with alumina; while chromite (natural chromite of iron), graphite, and plumbago are neutral in character, and bauxite, lime, magnesia, and zirconia are examples of basic refractories.

Fire-clay, being acidic in character, is destroyed when heated with bases such as lime; and magnesia, being basic, is destroyed when heated with an acid refractory such as clay.

Mica, talc, alumina, and carborundum are other refractories.

The mineral chromite is largely used in the manufacture of bricks for lining steel and copper smelting furnaces. These usually contain about 33 per cent. chromic oxide, with less than 6 per cent. of silica, the bricks being compounded by mixing the powdered ore with water and a binding material (such as tar) into paste form, followed by moulding, drying, and burning up to  $1,460^{\circ}\text{C}$ . in kilns.

Refractory mortars and cements employed for joining, patching, or binding, and as washes over surfaces, are sometimes made of corresponding materials, namely, silica, rock, fire-clay, ganister, and silica brick ("grog"), but are made up to be slightly more fusible than the materials to be treated, so that a vitrified bond is formed upon the application of strong heat. The chief bonding agents are ball-clay, lime, Portland cement, sodium silicate, and ground glass.

Zirkite cement consists wholly of zirconia, finely ground and made into a paste with water. Silica bricks are generally used in the construction of electric furnaces.

In his work on *Refractories*, by A. B. Searle, it is stated that fire-bricks heated in a darkened chamber (as in a kiln) exhibit the appearances noted below at various given temperatures:

Just-visible red	..	..	..	$500^{\circ}$ to $650^{\circ}\text{C}$ .
Cherry red	..	..	..	$850^{\circ}$ to $900^{\circ}\text{C}$ .
Bright red	..	..	..	$1,000^{\circ}\text{C}$ .
Orange	..	..	..	$1,100^{\circ}\text{C}$ .
Yellow	..	..	..	$1,200^{\circ}\text{C}$ .
White	..	..	..	$1,500^{\circ}\text{C}$ .

and that they begin to lose their shape when the temperature reaches to from  $1,600^{\circ}$  to  $1,800^{\circ}\text{C}$ . "Spalling" of fire-brick is defined as fracture or disintegration caused by rapid changes in temperature.

The sensitiveness of a fire-clay to load is the greater, the greater the alumina content of the clay, and conversely it decreases as the silica content increases. The loss of mechanical strength of coarse-grained silica bricks at high temperatures is much less than that of fire-clay bricks. All refractory products become more or less plastic beyond  $1,200^{\circ}\text{C}$ ., no abrupt rupture then taking place. Physical tests, especially the heat conductivity, are of great importance in the examination of refractories.

A silica brick containing over 97 per cent. silica is stated to be universally used in the United States on account of its great resistance to high temperatures, so that from 2,350° to 2,550° F. can be used, and even 2,700° to 2,900° F. for limited periods, this being some 400° to 475° F. higher than that which can be employed with ordinary fire-bricks. These bricks exhibit greater conductivity at high temperatures, and are more resistant to the corrosive action of salt.

Electrically sintered magnesite, containing 95 per cent. MgO and less than 1 per cent. iron oxide, as produced in the United States, is non-contractile and particularly resistant to high temperatures (having a melting-point of about 2,600° C.), thus making it valuable for lining metallurgical furnaces, etc.

(See "Properties of Various Refractories," by H. Kothny (*Ind. Chem.*, 9, 239 (1933)); *A Comprehensive Treatise on Refractories*, by A. B. Searle (C. Griffin and Co., London); *Refractories*, by F. H. Norton (McGraw-Hill Book Co., New York); Bricks, Clays, Poreclain, Saggars, Sillimanite, and Sintering.)

**REFRIGERATION** — There are processes for refrigerating perishable and other articles, based upon the cooling which is produced by causing volatile liquids like strong ammonia and liquefied carbon dioxide to assume the vaporous state. This change of state involves the absorption of heat, and can thus be made available for the construction of cooling machines for foods and industrial uses, such as the concentrating of penicillin (see same) by "freeze-drying."

The machinery involved in mechanical refrigeration is of two classes, namely, compression and absorption.

Compression machines can use a variety of refrigerants, of which the principal are listed in the accompanying table.

#### PROPERTIES OF REFRIGERANTS AT ATMOSPHERIC PRESSURE

			Boiling Point ° C.	Latent Heat of Vaporization Calories per Gram
Diethyl ether	..	..	35	84
Freon 11 (CCl <sub>3</sub> F)	..	..	24	44
Ethyl chloride	..	..	13	93
Freon 21 (CHCl <sub>2</sub> F)	..	..	9	57
Freon 114 (C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub> )	..	..	3	32
<i>n</i> -Butane	..	..	0	92
Sulphur dioxide	..	..	-10	95
Isobutane	..	..	-10	88
Methyl chloride	..	..	-24	102
Freon 12 (CCl <sub>2</sub> F <sub>2</sub> )	..	..	-30	40
Ammonia	..	..	-33	327
Propane	..	..	-42	102
Carbon dioxide	..	..Subl.	-79	89
Ethane	..	..	-90	258

Absorption machines have hitherto used ammonia and water, but the Platen-Munters continuous absorption system, embodied in the "Electrolux" household refrigerator, employs ammonia, water, and hydrogen. It has no moving parts and requires only heat and cooling water.

For larger refrigerators the compression system is to-day preferred. Compression machines are said to be more flexible and less bulky than the absorption type. Compressors may be reciprocating or rotary, and single or multi-stage according to the size of the plant and the nature of the refrigerant.

Commercial refrigerating capacity is measured in "Tons," nominally representing the weight of ice that could be made in 24 hours. In the U.S.A. the standard commercial "Ton of Refrigeration" corresponds to a cooling rate of 200 B.Th.U. per minute. The British Standard Unit corresponds to 237.6 B.Th.U. per minute (=1 kg.-cal. per second) between  $+15^{\circ}$  and  $-5^{\circ}$  C.

It is stated that cork slab stands first amongst insulators in refrigeration technique, while other combinations are made from cork and peat encased with tar. The thermal conductivity of cork slab through the temperature range ordinarily observed in cold storage is 0.28 to 0.33 B.Th.U. per square foot per hour per 1 inch thickness for  $1^{\circ}$  F. difference of temperature between the faces.

The opinion has been expressed by J. S. F. Gard that compressed cork in sheet or pipe sections is the best material for insulation for low temperature ranges, and a blended mixture of basic magnesium carbonate and asbestos for medium temperature ranges. Glass wool, slag wool, diatomaceous earth, pumice, and cotton waste are also used.

As to the preservation of meat and fish, it has been shown that, by sufficiently rapid cooling to a sufficiently low temperature the separation of crystals of water is avoided, and the cell walls are not ruptured. Upon thawing, the system returns to its original state.

The most important factor concerning the preservation of food is temperature, research having shown that in respect of living systems such as fruit and eggs it is best to employ one slightly above freezing-point, whereas with dead foodstuffs such as meat the chief aim is to restrict the action of moulds and bacteria and to control the extent of structural change. Temperature, humidity, and the composition of the air have all to be controlled.

Solid carbon dioxide has all the desirable properties of ice, its specific gravity is 1.5, and when it can be used, has great advantages over ice, 100 pounds doing the work of nearly a ton of ice. (See description of Dry Ice in article on Carbon Oxides.)

Processes of refrigeration are often used in chemical investigations, and there are many kinds available. Boiling methyl chloride as a frigorific gives a temperature of  $-23^{\circ}$  C., and solid carbon dioxide in ether or alcohol gives one of  $-75^{\circ}$  C., while liquefied air has given the means of liquefying hydrogen and helium.

See J. S. Beamensderfer on "The Common Refrigerants" (*Ind. Eng. Chem.*, **27**, 1027 (1935)); Thomas Midgley, Jr., on "Safe Re-

frigerants" (*Ind. Eng. Chem.*, **29**, 241 (1937)); *Refrigeration in the Chemical Industry*, by G. W. Daniels (Chapman and Hall, Ltd.); *Refrigeration, Theory and Application*, by H. G. Venemann (Nickerson and Collins, London); *Proc. Inst. Mech. Engrs.*, **143**, 261 (1940) for bibliography on Refrigerants; Perry's *Chemical Engineers' Handbook* (McGraw-Hill Book Co., New York); Eutectic, Foods, Heat (Latent Heat), and Heat Transfer (for insulating materials.).

**REGELATION** — The freezing of water anew, brought about by reduction of pressure, the melting-point of ice ( $0^{\circ}$  C. under pressure of 1 atmosphere) being affected by the alteration of pressure to a slight extent; thus, two pieces of ice, when rubbed together, melt at the surfaces and form into one mass upon relieving the pressure.

**REGULUS METAL** — Metallic alloys reduced to a crude state from oxides or other compounds by fluxing with reducing agents. Four types are recognized by the B.S.I. (B.E.S.A.). (See Ores.)

**REICHERT-WOLLNY VALUE** — See Fats.

**REINSCH'S TEST FOR ARSENIC** is based upon the fact that if a clean strip of copper be boiled in an acidified arsenical solution, a deposit of copper arsenide ( $\text{Cu}_3\text{As}_2$ ) forms on the surface.

**RENNET (RENNIN)** — An infusion of the inner membrane of the fourth stomach of the calf, soluble in salt water and used for coagulating milk in cheese-making. This coagulation is due to the action of an enzyme (contained in the rennet) of a class different from the enzymes which act by hydrolysis or oxidation, and is regarded by some as a decomposition product of protein of the acid albumin class. It readily diffuses through a parchment membrane and is not precipitated by heat. Several methods of preparing it are given in Jean Effront's *Bio-chemical Catalysts* (Chapman and Hall, London).

**RESINATES** — Compounds of the acid constituents of resin. The alkaline resinates known as "resin soaps" are largely used in sizing paper; for incorporation with ordinary soaps; the preparation of inks, paints, dopes; making polishes for wood and leather; as lubricants, and as substitutes for linseed oil in respect of certain applications. Resinate of sodium is made by digesting resin up to 47 per cent. in hot caustic soda solution, the product being a viscid cream or paste, as desired, which is miscible with water. Other resinates are obtained by chemical reaction between such solutions and metallic salts.

The partial (fused) resinates obtained by fusion of resin with metallic salts or oxides are extensively employed in compounding printing inks, also as siccatives for the drying of oils (owing to their solubility in linseed oil at comparatively low temperatures) instead of heating the oils at  $180^{\circ}$  C. with the oxides of lead or manganese. Those made by fusion always contain some free resin, and the use of such acid resinates is apt to lead to difficulties in the manufacture of paints, lacquers, and dopes when mixed with mineral colours, particularly those of zinc and

lead, whereas with the true resinates these difficulties are not encountered. The fused resinates are not completely dissolved by turpentine, "Tetraline," and some other solvents, but the partial solutions are used to some extent as liquid driers for paints and varnishes.

**RESIN OIL** — See Rosin Oil.

**RESIN SIZE** — See Rosin Size.

**RESIN SPIRIT** — See Rosin Spirit.

**RESINS** — See Gums and Resins.

**RESINOIDS** — See Gums and Resins (Synthetic Resins).

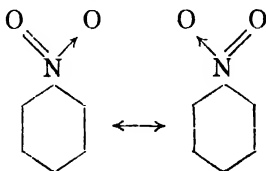
**RESONANCE** is the dynamic state of equilibrium existing when an entity which can exist in more than one possible configuration oscillates between its various forms. For example, in the ground state of the helium atom both electrons (outside the nucleus) presumably have the same energy; in this formation of the spectrum an excited state must be involved, and in this condition the electrons have different energies, but there is evidence that this excitation energy oscillates between the two electrons rather than remaining with just one electron. This resonance gives rise to new energy configurations for helium such as an *ortho* and a *para* configuration.

In organic chemistry resonance appears to play an important role. The heat of formation of benzene is 39 kilocalories greater than that calculated from the pure Kekulé structure. Also, the C—C interatomic distances (1.39 A.U.) in benzene are intermediate between those in paraffin compounds (1.54 A.U.) and in C=C olefin compounds (1.32 A.U.). It is believed that these two observations are best explained by resonance between the two structures:



where the sign  $\leftrightarrow$  represents resonance not equilibrium ( $\rightleftharpoons$ ) and the resultant structure is intermediate between the two shown.

The nitro group has one double bond to oxygen and a co-ordinate to the other oxygen atom, but the share of *each* of the two oxygen atoms is equal in *each* kind of bond, due, it is believed, to resonance. Nitrobenzene may be represented thus:



and here again the *resultant structure* is intermediate between the two shown.

**RESORCINOL (RESORCIN)** ( $C_6H_4(OH)_2$  (1, 3)) — A white crystalline dihydric phenol prepared from benzene-1, 3-disulphonic acid by fusion with excess of sodium hydroxide. It is soluble in water, alcohol, ether, glycerin, and olive oil; m.p.  $110^\circ C.$ , b.p.  $276^\circ C.$  It is used in medicine as an antiseptic for external application, and in the preparation of several dyes. On treatment with nitrous acid, resorcin yields dinitrosoresorcinol (Alsace Green). It can also be used as a solvent in printing pastes containing basic dyestuffs, thus dispensing with the usual steaming process.

**RESPIRATION** is essentially a chemical process whereby the blood is purified by absorption of oxygen from the air breathed into the lungs; nitrogen, carbon dioxide, and aqueous vapour being exhaled. The exhaled breath contains about 4.4 per cent. of carbon dioxide and 16.4 per cent. oxygen as compared with 0.04 per cent. of the former and 21.0 per cent. of the last-named substance contained in the inhaled air, together with moisture, traces of ammonia, and some organic matters that make overcrowded or ill-ventilated rooms unpleasant and unhealthy.

The inhaled oxygen of the air enters into a loose combination with the hæmoglobin of the blood corpuscles and is thus carried to all parts of the living tissues, which in their turn give up carbon dioxide, water, urea, and other excrementitious products which are carried away in the breath and urine. It has been estimated that 1,000 c.c. of healthy human blood may contain a maximum of 240 c.c. oxygen (measured as separate gas). (See Hæmatine.)

When air contains from 2.5 to 3 per cent. carbon dioxide, breathing is adversely affected, and becomes distressful when 4 per cent. is reached, while with a content of 5 per cent. distress becomes acute.

The water given off in the exhaled breath in twenty-four hours has been estimated at nearly 11 ounces, and the carbon (as carbon dioxide) at from 7.1 to 11.7 ounces.

An excellent account of respiration is given in *Noxious Gases and the Principles of Respiration Influencing their Action*, by Yandell Henderson and H. W. Haggard (Reinhold Publishing Corp., New York).

**RESPIRATORS** — See Gassing.

**RETENE** ( $C_{18}H_{18}$ ) — A hydrocarbon (methylisopropylphenanthrene) accompanying pyrene, etc., in the coal-tar distillate which comes over above  $360^\circ C.$ , and used as a source of dyestuffs. (See Pyrene.)

**RETORTS (Still)** — Apparatus made of glass, earthenware, iron, steel, platinum, etc. (according to the chemical characteristics of the materials to be dealt with), variously used for the separation of the more volatile parts of liquid or solid mixtures and for "cracking" or so-called destructive distillation of tar, petroleum, and other substances, etc. The retorts for roasting coal in the process of gas-making and other industrial operations are constructed on the same principle as laboratory retorts, coupled with cooling arrangements (condensers) for condensing the distillates.

**RETTING** — Soaking, macerating, or wetting. (See Flax.)

**REVERBERATORY FURNACE** — See Furnaces.

**REVERSIBLE REACTIONS** — See Chemical Interactions.

**RHAMNICOSIDE** — See Glycosides.

**RHAMNOSE** ( $C_6H_{12}O_5 \cdot H_2O$ ) — A colourless, crystalline carbohydrate, a methylpentose, being 6-desoxy-*l*-mannose. It is obtained by hydrolysis from several glycosides, especially those occurring in certain species of the genus *Rhamnus*. M.p.  $126^\circ C$ . (See Frangula, and Quercitrin.)

**RHAMNOSIDES** — Glycosides which yield rhamnose upon hydrolysis.

**RHATANY ROOT** — See Krameria.

**RHENANIA PHOSPHATE** — See Leucite.

**RHENIUM** (Re) and its Compounds — Atomic weight, 186.31. See Elements for other data. Rhenium is found in certain molybdenum ores, and is frequently present in manganese preparations. From molybdenite, rhenium is obtained by treatment with nitric acid, separation of the molybdenum by precipitating as phosphomolybdate, and recovery of rhenium from the filtrate by precipitation with hydrogen sulphide. This product is oxidized, and the resulting sublimed rhenium heptoxide is then heated in a current of hydrogen gas and reduced to rhenium metal.

There are three **oxides** of rhenium, namely, the heptoxide ( $Re_2O_7$ ), a yellow solid; the dioxide ( $ReO_2$ ), a black solid; and the tetroxide or peroxide ( $ReO_4$ ), a white solid. All of these are formed by heating rhenium in a current of oxygen gas.

**Rhenium Chloride** ( $ReCl_4$ ) is a black liquid of b.p.  $500^\circ C$ . There are two **sulphides** of rhenium, namely, the disulphide ( $ReS_2$ ); and the heptasulphide ( $Re_2S_7$ ), which latter is a black solid, formed by reaction of potassium perrhenate and hydrogen sulphide.

**Potassium Perrhenate** ( $KReO_4$ ), stable in acid solution, and reducible in acid solution by iodide, is colourless in marked contrast to potassium permanganate. It is an article of commerce.

Rhenium compounds impart a pale green colour to the Bunsen flame. (See *Rhenium*, by J. G. F. Druce (Cambridge Univ. Press).)

**RHEOLOGY** — Study of the flow of matter as related to plasticity, viscosity, and elasticity.

**RHIZOME** — Underground stems or rootstock.

**RHODAMINES** — A series of xanthene dye-bases related to fluorescein, being colourless bodies of which the salts, such as the sulphate, are red.

**RHODINOL** ( $C_{10}H_{18}OH$ ) — An alcoholic body occurring in the essences of rose and geranium. It can be prepared synthetically from beta-geraniol. (See Jacobs in *Amer. Perfumer*, 48, No. 9, 54 (1946).)

**RHODIUM** (Rh) and its Compounds — Atomic weight, 102.91. See Elements for other data. Rhodium is found in platinum ores to the extent of about  $\frac{1}{2}$  per cent., and belongs to the platinum group. It is white, lustrous, has a melting-point much above that of platinum, and is used in the construction of electrical pyrometers.

There are three **oxides** of rhodium, namely, the dioxide ( $RhO_2$ ); the sesquioxide ( $Rh_2O_3$ ); and the monoxide ( $RhO$ ).

**Rhodium Chloride** ( $\text{RhCl}_3 \cdot 4\text{H}_2\text{O}$ ) is a dark red solid.

There are two **sulphides** of rhodium, namely, the monosulphide ( $\text{RhS}$ ); and the sesquisulphide ( $\text{Rh}_2\text{S}_3$ ), blue-white and black solids, respectively.

**Rhodium Sulphate** ( $\text{Rh}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$ ) is a light yellow crystalline solid.

**RHODIUM (Rosewood)** — The wood of *Convolvulus scoparius* and *C. floridus*, etc. (from Canary Islands and West Indies), containing an oil (0.04 per cent.) used in perfumery and for baiting the fox, etc. The wood is also used by cabinet-makers and pen manufacturers.

**RHODONATE** — Thiocyanate.

**RHUBARB (Rheum)** — The dried rhizome of *Rheum palmatum* and possibly other species of *Rheum*, except *Rheum rhaponticum*, which are cultivated in China and Thibet. After collection, the rhizome is stripped of most of its bark and dried. Different varieties are known in commerce as Shensi, Canton, and high-dried rhubarb. It contains derivatives of anthraquinone and is used in medicine as a purgative. Rhapontic rhubarb, derived from *R. rhaponticum*, contains a glycoside, rhaponticin, and can be distinguished by the bright violet or lilac fluorescence it exhibits under ultra-violet light.

**RHUS (Sumac)** — There are many species rich in tannic acid. (See Sumac.)

**RIBOFLAVIN** — See Vitamins.

**RICE** — A well-known grain (*Oryza sativa*), being the only important species of a genus of grasses (of which the chief constituent is starch) largely grown in Asia, South America, and the United States, the chief producing countries being India and China. The sp. gr. of rice is about 1.43 to 1.46, and the flour contains from 73 to 79 per cent. starch, associated with fat varying from 0.5 to 1 per cent., albuminoids (chiefly protein) from 7 to 8.5 per cent., water about 13 per cent., and small proportions of mineral and other substances. Polishing decreases the nutritive properties of rice. The polishings contain oil of sap. v. 185.3, i.v. (Hanus) 99.9, Reichert-Meissl v. 0.3, Polenski v. 0.3, ref. ind. 1.469 at 25° C., and acid v. 73.7 (see G. S. Jamieson, *Analyst*, 51, 583 (1926)). The polishings are usually sold as a fertilizer or feeding-stuff, while rice hulls are now also used as a source of cellulose.

Analyses of rice from the Philippine Islands and the U.S.A. respectively have been published as follows:

	Philippines	United States
Weight of 100 kernels (in grams) ..	1.97	2.46
Moisture (per cent.) .. ..	12.26	11.88
Protein (per cent.) .. ..	7.93	8.02
Ether extract (per cent.) .. ..	2.03	1.96
Crude fibre (per cent.) .. ..	1.18	0.93
Other carbohydrates (per cent.) ..	75.89	76.05
Ash (per cent.) .. ..	1.46	1.15
Phosphorus pentoxide (per cent.) ..	0.75	0.40

Rice bran contains about 13 to 15 per cent. fat, and owing to this and its porosity it becomes rancid by storage. The wax in rice polishings is alleged to be melissyl cerotate. (See Starch, and Vitamins.)

**RICIN (Ricinine)** ( $C_8H_8O_2N_2$ ) — An alkaloid obtained from the castor bean, being a derivative of dihydropyridine. It is toxic and is present, after expression of the oil, in the seed-cake, which may not therefore be used as an animal fodder.

**RICINOLEIC ACID** ( $C_{17}H_{32}(OH)COOH$ ) — The glyceride of this fatty acid (triricinolein) makes up some 82 per cent. of castor oil, and occurs also in curcas oil. The acid is yellowish, thick, m.p.  $4^{\circ}C.$ , sp. gr. 0.954; i.v. 85.39; acid v. 188.1; soluble in alcohol, ether, etc.; resembles oleic acid in properties, and is used in soap-making, manufacture of Turkey-red oils, and dressing of textiles. (See Castor Oil.)

**RIMU OIL** — A volatile oil obtained from the leaves of the red pine, *Dacrydium cupressinum*, a tree growing in the forests of New Zealand. It contains a solid crystalline diterpene,  $C_{20}H_{32}$ , melting at  $55.5^{\circ}C.$

**RINGS** — Collections of atoms arranged in ring form, such as the benzene ring. The international rules for numbering organic ring systems by the Committee on Organic Nomenclature of the International Union of Pure and Applied Chemistry are given in *The Ring Index*, by Austin M. Patterson and L. T. Capell (Reinhold Publishing Corp., New York); and selections are presented in *Handbook of Chemistry*, by N. A. Lange (Handbook Publishers, Sandusky, Ohio). (See Benzene Ring, Chains, Cyclic, Heterocyclic, Homocyclic, and Nomenclature.)

**RITHA (Sajji)** — An Indian soap substitute, consisting of an alkaline deposit found on certain waste lands.

**RITTINGER'S LAW** — See Crushing.

**ROASTING (Ores)** — See Furnaces, Pyrites, and Ores.

**ROBURITE** — See Explosives.

**ROCHELLE SALT** ( $KNaC_4H_4O_6 \cdot 4H_2O$ ) — A double tartrate of potassium and sodium, being a colourless crystalline compound, soluble in water, used in the preparation of Seidlitz powders and certain baking-powders. It loses its water of crystallization at  $215^{\circ}C.$  It is used in the preparation of Fehling's solution in order to obtain copper in alkaline solution (as complex cupric tartrate ion).

**ROCK CRYSTAL** — See Silicon.

**ROCK PHOSPHATES** — See Phosphates, Phosphorus, and Iron (Slag).

**ROCK SALT** — See Sodium.

**ROCKS** — A rock is "any mineral or aggregate of minerals that forms an essential part of the earth," and shows "a well-marked individuality" (Kemp). Important rock-forming minerals are quartz, feldspar, hornblende, pyroxene, mica, kaolin (clay), limestone, gypsum, hematite, bauxite, rock salt, and ice. These may be loose and incoherent, or

dense and hard. The predominant minerals of the igneous rocks of the earth's crust are estimated by F. W. Clarke as follows :

Feldspar .. .. .	59.5 per cent.
Hornblende and pyroxene ..	16.8 "
Quartz .. .. .	12.0 "
Biotite .. .. .	3.8 "
Total	92.1 "

The predominant elements—expressed as oxides—of the igneous rocks are estimated by the same writer as follows:  $\text{SiO}_2$ , 60 per cent.;  $\text{Al}_2\text{O}_3$ , 15 per cent.;  $\text{Fe}_2\text{O}_3$ , 2.7 per cent.;  $\text{FeO}$ , 3.5 per cent.;  $\text{CaO}$ , 4.8 per cent.;  $\text{MgO}$ , 3.8 per cent.;  $\text{Na}_2\text{O}$ , 3.4 per cent.;  $\text{K}_2\text{O}$ , 3.0 per cent. The igneous rocks are said to constitute 95 per cent., shale 4 per cent., sandstone, 0.75 per cent., and limestone 0.25 per cent. of the earth's crust (F. W. Clarke).

See *The Chemical Analysis of Rocks*, by H. S. Washington (John Wiley and Sons, New York); *The Data of Geochemistry*, by F. W. Clarke (U.S. Geol. Survey, Washington).

**RODENTICIDES** — Many substances have been used to kill rats and other noxious rodents, and the proper choice depends upon the circumstances of use. Frequently satisfactory kills may be obtained by mixing one of the violent poisons, such as strychnine, cyanide, phosphorus paste, or zinc phosphide with food materials. "Antu" ( $\alpha$ -naphthylthiourea) and "1080" (sodium fluoroacetate) are highly effective. The use of any of these materials is, however, attended by considerable danger, since children, pets, or domestic animals may be poisoned rather easily unless extreme care is exercised in the operation.

A more satisfactory rodenticide which is harmless to animals other than rats is red squill, derived from the dried bulbs of *Urginea maritima*, a plant growing in the Mediterranean coastal area. Mixed with meat, fish, or cereals, this affords a safe and effective means of exterminating rats. (See Squill.)

**ROENTGEN (R)** — The quantity of radiation that produces one electrostatic unit (e.s.u.) of electricity of either sign per cubic centimetre of air at standard temperature and pressure.

**ROMAN ALUM** — See Aluminium (Alums).

**ROMAN CEMENT** — A form of hydraulic cement, in making which septarian nodules are employed. (See Cement, and Septaria.)

**"RONGALITE"** — The name given to certain German reducing agents used in the dyestuffs and dyeing industries, said to be sodium formaldehyde-sulphoxylate and zinc formaldehyde-sulphoxylate, the last named being used for "stripping." (See "Zinc Formosul.")

**RÖNTGEN RAYS** — See X-Rays.

**ROPINESS (of Bread, Milk, Beer, etc.)** — A defect due to biological changes induced by certain micro-organisms. In bread, the cause is attributed to *Bac. mesentericus*; in milk, to certain lactic acid bacteria loosely referred to as *Bact. lactis viscosum*; and in beer, the defect is considered by some to be due to a *coccus* or *sarcina*, or possibly to bacteria of the acetic acid type.

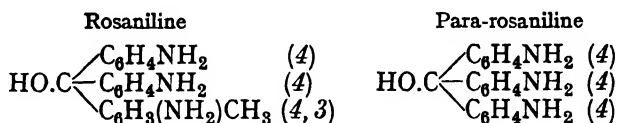
The best preventives are low temperature, ventilation, and cleanliness to the degree resulting in the absence of micro-organisms. The addition of lactic acid and acid potassium and calcium phosphates may inhibit ropiness. (See "Mycoban," and Wheat.)

**ROSANILINES** — The aminated bases of fuchsine or magenta dyes. The rosanilines are colourless, crystalline compounds, and only form dyes when united with an acid. Rosaniline ( $C_{20}H_{21}ON_3$ ) and para-rozaniline ( $C_{19}H_{19}ON_3$ ) are obtained by precipitation of their salts with alkalis.

The actual dyes are the salts of these compounds, and include magenta, otherwise known as fuchsine ( $C_{20}H_{20}N_3Cl$ ), rosaniline nitrate, ( $C_{20}H_{20}N_3(NO_3)$ ), rosaniline acetate ( $C_{20}H_{20}N_3(C_2H_3O_2)$ ), and para-fuchsine ( $C_{19}H_{18}N_3Cl$ ). These all dye wool and silk without a mordant, giving a magnificent fuchsine-red colour in solution, but are themselves in crystalline form of a bright metallic green lustre. They are soluble in hot water and alcohol.

Rosaniline yields rosolic acid by treatment with nitrous acid.

The formulas of rosaniline and para-rozaniline are :



**ROSCOELITE (Vanadium Mica)** — Contains at times up to 28 per cent. vanadium pentoxide.

**ROSE OIL** — See Attar of Roses.

**ROSEÏNE (Fuchsine)** — See Magenta, and Rosanilines.

**ROSELLE FIBRE** (cultivated in the Federated Malay States) is of a jute nature, but alleged to be stronger than jute.

**ROSEMARY (OIL OF)** — The volatile oil distilled from the leaves of *Rosmarinus officinalis* (Fam. Labiatæ), containing from 8 to 16 per cent. of bornyl acetate, with camphor, cineole, pinene, and camphene; soluble in alcohol and ether; sp. gr. 0.900 to 0.919 at 15° C.; opt. rot. -5° to +10° at 20° C.; ref. ind. 1.464 to 1.467 at 20° C.; used in perfumery and toilet preparations. The Sardinian, French, Dalmatian, Sicilian, and Spanish oils vary in their optical rotation and in the proportions of ingredients.

**ROSIN** — See Gums and Resins (Colophony).

**ROSIN OIL** — The fraction from the destructive distillation of rosin (colophony) which comes over after the rosin spirit, and up to about 400° C., constituting the bulk of the total distillate. It exhibits a blue fluorescence, and is a mixture of hydrocarbons, phenols, and free rosin acids ranging from 9 to 30 per cent. The last-named substances can be removed, together with some of the dark colour, by treatment with caustic soda. In general, it resembles mineral oil, and is of sp. gr. varying from 0.92 up to over 1.12. There are a number of grades, one of the refined quality being practically colourless (known as "pine oil"), while another of crude character is dark blue, and known as "blue rosin oil," or "blue billy." It is soluble in ether, turpentine, carbon disulphide, etc., and finds use as a lubricant and as an adulterant of boiled linseed and other oils. (See Rosin Spirit, and Wood (Distillation).)

**ROSIN SIZE (Resin Size)** — Ordinary rosin dissolved in alkali, used for sizing paper, etc.

**ROSIN SPIRIT (Pinoline)** is a complex mixture of hydrocarbons and rosin acids, forming the distillate from the destructive distillation of colophony that comes over at about 200° C., and amounting to from 2½ to 5 per cent. of the total distillate. It can be freed from associated acids by caustic soda, or refined by agitation with strong sulphuric acid and subsequent redistillation. When rectified, it has a sp. gr. of about 0.856 to 0.883, is miscible with petroleum spirit and turpentine, and is used as a solvent and substitute for turpentine in the paint and other trades. (See Rosin Oil, and Wood (Distillation).)

**ROSOLIC ACID** ( $C_{20}H_{16}O_3$ ) — A beautiful green-coloured crystalline substance with a metallic lustre and m.p. 270° C., chemically related to aurine and made by oxidation of phenol and cresol with arsenic and sulphuric acids. It is soluble in alcohol and ether, and is used in dyestuffs.

**"ROSTKITT"** — A rusting cement consisting of 85 parts iron filings, 10 flowers of sulphur, and 5 of sal-ammoniac stirred with water into a paste, its action resulting from the oxidation of the iron.

**ROTAMETERS** — Instruments for measuring the rate of flow of gases or liquids through a calibrated pipe, the fluid flowing upwards and lifting a float; used for the control of air in the bio-aeration method of sewage disposal, the control of chlorine for water purification, mixing gases in correct proportions, measuring liquids and solutions in motion, etc.

**ROTATORY POWER** — See Light (Polarization).

**ROTENONE** ( $C_{23}H_{22}O_6$ ) — A colourless, odourless, crystalline constituent of certain tropical fish-poison plants, and found in the devil's shoe string (*Cracca virginiana*), a common weed, and derris root (*Derris elliptica*). Rotenone is used in flea powders, fly sprays, greenhouse sprays, in mothproofing of wool and for combating ox warbles; is fifteen times as toxic as nicotine as a contact insecticide upon bean aphids, and thirty times as toxic as lead arsenate as a stomach poison to silkworm, but harmless to birds and mammals eating it; of m.p.

163° C. ; sp. gr. 1.27 at 20° C. ; strongly lævo-rotatory in solution, e.g., specific rotation for D line -230° in benzene, -62° in ethylene dichloride.

See H. D. Lightbody and J. A. Mathews on "Toxicology of Rotenone" (*Ind. Eng. Chem.*, **28**, 809 (1936)) ; J. A. Mathews and H. D. Lightbody on "Toxicity of Derris and Cube" (*Ind. Eng. Chem.*, **28**, 812 (1936)) ; A. M. Ambrose and H. G. Haag on "Toxicological Study of Derris" (*Ind. Eng. Chem.*, **28**, 815 (1936)) ; *Chemistry of Insecticides and Fungicides*, by D. E. H. Frear (D. Van Nostrand Co., New York) ; Insecticides, and Dihydrorotenone.

**ROTTEN STONE** — A mineral powder, a disintegrated rock of limestone nature, found near Bakewell in Derbyshire and elsewhere, containing a large proportion of alumina ; highly prized for polishing brass, etc.

**ROUGE** — A common name for a finely divided form of ferric oxide, employed as a pigment and for polishing glass, etc. ; prepared by heating ferrous sulphate. (See Iron (Ferric Oxide).)

**RUBBER, NATURAL and SYNTHETIC** — The rapid advance of the Japanese military forces through Malaya in 1942 changed the rubber technology of the world markedly through the elimination of crude rubber, and forced the substitution of synthetic elastomers. The change from natural to synthetic rubber upset a situation that had developed steadily from the time that H. A. Wickman and his colleagues brought the *Hevea brasiliensis* seeds from Brazil to London, thence to the East Indies. (*On the Plantation, Cultivation and Curing of Para Indian Rubber* (London, 1908).) This disturbance is approaching an equilibrium between natural and synthetic rubbers, each finding its most useful places, or being eliminated in the competition. *Hevea* rubber accounts for more than 95 per cent. of the crude rubber produced in the world, the remainder coming from African *Landolphia*, Asiatic *Ficus elastica*, and North American *Guayule*. All the natural rubbers contain resins, but in the *Hevea* product the resin content has been reduced to a minimum by careful selection and breeding.

The synthetic rubber industry is centralized in the United States, partly as a result of the work of Father Nieuland and Wallace Carothers, but mostly as a result of necessity following the Japanese conquest of Malaya. A synthetic rubber had been made in Germany (*circa* 1917) from methylbutadiene but it was not satisfactory. A concentrated drive by the combined scientific staffs of the rubber companies of the Allied Nations produced a synthetic rubber from butadiene and styrene (GR-S, Government Rubber from Styrene). This synthetic rubber proved satisfactory for tyres and many mechanical goods. Later developments included GR-I (Government Rubber from Isobutylene) also known as "Butyl," and GR-A (Government Rubber from Acrylonitrile).

Butyl (GR-I) is made from 2 per cent. isoprene and 98 per cent. isobutylene, and is extensively used in automobile inner tubes because of its low air permeability.

GR-A is made from butadiene and acrylonitrile and is noted for its excellent resistance to paraffin oils. The well-known "Neoprene" was the first of the oil-resistant rubbers. It is made from chloroprene (Carothers, *Ind. Eng. Chem.*, **26**, 30 (1934)).

See *B.I.O.S. Overall Report on the Rubber Industry in Germany 1939-1945* (H.M. Stationery Office, London).

#### PROBABLE STRUCTURE OF ELASTOMERS

Name	Source	Formula
Natural	<i>Hevea brasiliensis</i>	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \end{array} \right]_x$
GR-S	Butadiene and Styrene	$\left[ -\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}(\text{C}_6\text{H}_5)-\text{CH}_2- \right]$
GR-A	Butadiene and Acrylonitrile	$\left[ -\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\underset{\text{CN}}{\text{CH}}-\text{CH}_2- \right]_x$
GR-I	Isobutylene and Isoprene	$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{CH}_3 \\   \qquad \qquad \qquad   \\ -\dot{\text{C}}-\text{CH}_2-\text{CH}_2-\dot{\text{C}}=\text{CH}-\text{CH}_2- \\   \\ \text{CH}_3 \end{array}$
Neoprene	Chloroprene	$\begin{array}{c} \text{Cl} \\   \\ -\text{CH}_2-\dot{\text{C}}=\text{CH}-\text{CH}_2- \end{array} \left]_x$
Thiokol	Dichlorohydrocarbons and Sodium Polysulphide	$\left[ -\text{CH}_2-\text{CH}_2-\text{S}- \right]_x$

The compounding of rubber mixtures has been complicated by the variety of specialized elastomers, but improved results are evidenced by the superior qualities of the synthetics in certain fields. Natural rubber and each synthetic has its own place in the technical field, and in many cases they are not competitive.

**Natural Rubber**—The latex is obtained from the *Hevea brasiliensis* tree by tapping, whereby a system of grooves opens the laticiferous structure of the tree and allows the latex to drain into appropriately placed cups. The collected latex is preserved with ammonia, sodium hydroxide, or similar basic substances. When the latex is to be made into dried rubber it is coagulated by use of acidic substances and the

K.C.E.—30

coagulum washed and dried, but if steam heat is used in drying, pale crepe type of rubber is made. Most of the coagulum is, however, dried in the smoke of native woods, resulting in smoked sheet rubber. Each of these types has various grades, depending upon the purity and cleanliness.

The juice of the rubber plant contains 30 to 36 per cent. rubber, and, as collected, is a thick creamy substance that has a marked tendency to ferment. The tendency is commercially prevented by the use of ammonia. Caustic soda, sodium carbonate, sodium sulphite, and other materials have also been used for this purpose.

According to K. Gortner, *Hevea* latex from trees thirty-five years old contains per litre 370 grams caoutchouc, dry matter in serum 29.1 grams, including 5.3 grams ash, 3.4 grams protein, 14.5 grams quebrachitol, 2.5 grams sugar, and 3.4 grams unascertained matter (*J. Chem. Soc., Abs.*, **128**, 622 (1925)). Undiluted *Hevea* latex containing less than 17 per cent. rubber may have a density greater than water.

A. J. Atlee found that the dry alcohol coagulum from the latex of *Ficus elastica* yielded 96.2 per cent. caoutchouc; that from *Castillio elastica* 84.9 per cent.; *F. vogelli* 72.9 per cent.; *F. glomerata* 16.6 per cent.; *F. procera* 12.1 per cent.; *F. vulva* 1.1 per cent.; and *F. alba* only a trace (*Brit. Chem. Abstracts, A*, **1926**, 1066).

A patented process of manufacture depends upon the electrolytic anodic deposition of rubber from latex, either natural or synthetic, the anode serving as the mould. (See S. E. Sheppard, *Brit. Chem. Abstracts, B*, **1927**, 852; P. Klein, *Chem. Trade J.*, **83**, 511 (1928); "Rubber-lined Equipment," by J. R. Hoover and H. C. Klein, *Ind. Eng. Chem.*, **29**, 394 (1937).)

The latex may be shipped without coagulation if properly preserved, and is then called normal latex. Concentrated latex is made by evaporation, by centrifuging, or by creaming. Either type can be used in the "Anode" process of electric deposition, or in the dipping process employing a coagulant on the form. Moulded goods are made from latex by the use of gelling agents. Sodium fluosilicate is widely used to obtain a rapidly setting gel. The nitroparaffins and nitro-alcohols have been described (Campbell, *Ind. Eng. Chem.*, **34**, 1106 (1942)) for high-temperature gels. These nitro-alcohols produce systems that have the advantage of being stable at room temperature and gelling readily at 80° C.

**Synthetic Rubber** — Butadiene is the common constituent of all synthetic rubbers, excepting "Neoprene" and "Butyl," and even in these the fundamental structure of butadiene is present. The butadiene is made from two sources, namely, industrial ethyl alcohol and petroleum. The GR-S rubber requires styrene, which is made from benzene ( $C_6H_6$ ) and ethylene ( $CH_2:CH_2$ ), the resulting ethylbenzene ( $C_6H_5CH_2CH_3$ ) being dehydrogenated to styrene ( $C_6H_5CH:CH_2$ ) under the proper conditions. There were no facilities for the manufacture of butadiene in 1942, but plants were rapidly constructed. Styrene in small amounts was commercially available, and plants for

its production were set up rapidly. (See *J. Amer. Chem. Soc.*, **68**, 1422 (1946); *J. Polymer Sc.*, **1**, 275, 318 (1946); *Ind. Eng. Chem.*, **38**, 975 (1946); *J. Amer. Chem. Soc.*, **68**, 1429 (1946); *Synthetic Resins and Rubbers*, by Paul O. Powers (John Wiley and Sons, New York); *Principles of High Polymer Theory and Practice*, by A. X. Smith and C. A. Marlies (McGraw-Hill Book Co., New York); *Natural and Synthetic Rubbers*, by Wildschut (Elsevier Publishing Co., New York).)

**Cold Rubber** — The discovery of new initiators of polymerization has made it possible to conduct emulsion polymerization at low temperatures (below 0° C.), for example, the copolymerization of butadiene and styrene in the presence of an equal amount of *n*-butane. Elastomers have been produced in this way with monomers such as the acrylates and methacrylates. This development gives promise of remarkable results with respect to resistance to flexing and abrasion. A combination of "cold" rubber and special furnace type (HAF) carbon black (see same) has shown an increase of 40 per cent. in the life of tyres over the conventional natural or GR-S rubber. The infra-red absorption spectrum indicates that "cold" rubber has a trans structure in contrast to cis for natural and a mixture of cis and trans for G-RS.

## RUBBER SITUATION IN 1947

Country	Production (long tons)			Consumption (long tons)		
	Natural	Synthetic	Total	Natural	Synthetic	Total
Malaya.. ..	646,000	—	—	—	—	—
Indonesia ..	295,000	—	—	—	—	—
Ceylon .. ..	89,000	—	—	—	—	—
Indo-China ..	38,000	—	—	—	—	—
U.S.A. . . .	—	509,000	—	563,000	560,000	1,123,000
Canada .. ..	—	42,000	—	32,000	29,000	61,000
United Kingdom	—	—	—	154,000	3,000	157,000
France .. ..	—	—	—	61,000	13,000	74,000
Germany .. .	—	8,000	—	8,000	8,000	16,000
Netherlands ..	—	—	—	8,000	—	8,000
Other European	—	—	—	98,000	13,000	111,000
Australia .. .	—	—	—	23,000	—	23,000
Rest of World	—	—	—	185,000	30,000	215,000
Total .. ..	1,068,000	559,000	1,627,000	1,132,000	656,000	1,788,000

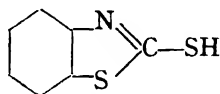
**Vulcanization** — In general, the combination of sulphur and rubber is regarded as vulcanization (*J. Polymer Science*, **1**, 293, 305, 312 (1946)), but oxygen can produce compositions that simulate the properties of the vulcanized-rubber-sulphur compositions. The best results are obtained when a basic metallic compound like zinc oxide, sulphur, and an accelerator (described later) are intimately mixed with rubber and heated. Sulphur alone is by far the most widely used vulcanizing agent; however, tetralkylthiuram disulphide (*Trans.*

*Inst. Rubber Ind.*, **22**, 189 (1946)) without free sulphur produces vulcanizates, being itself the vulcanizing agent. The vulcanization reaction is always exothermic.

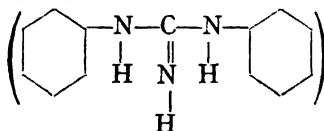
Cold vulcanization can be obtained by the use of sulphur chloride ( $S_2Cl_2$ ) in benzene solution, by hydrogen persulphide, or by sulphur and ultra-accelerators.

For reference to Soft Rubber Vulcanization see *Ind. Eng. Chem.*, **25**, 1042, 1292 (1933); **26**, 434 (1934); **29**, 208 (1937).

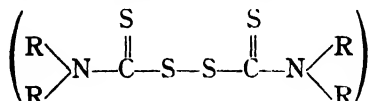
**Accelerators** — Accelerators involve organic compounds that greatly increase the rate of vulcanization. Some inorganic compounds, *i.e.*, litharge and lime, behave similarly, but this usage of inorganic compounds is being abandoned. The most widely used compound is mercaptobenzothiozol (Captax)



with numerous modifications and derivatives. Diphenylguanidine

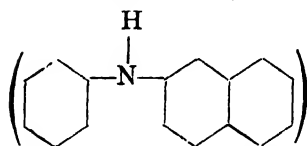


was a favourite accelerator in the early days, and continues to be extensively used. The thiuramdisulphides



constitute the ultra-accelerators, with the tetramethyl compound most extensively used. The tetraethyl compound is also used. The zinc salt of dimethyl and di-*n*-butyl dithiocarbamate is used in very specialized cases, such as self-curing cements and latex compositions.

**Antioxidants** — These are organic materials that markedly increase the service life of many rubber compositions. Phenylbetanaphthylamine



is the most widely used, and various

other secondary amines in specialized cases. As in the case of accelerators and loading agents, the proper antioxidant must be selected for the service for which the specific composition is designed. Flex- and abrasion-resistant compounds must be treated differently from those subjected to heat or oil (R. A. Crawford, *Ind. Eng. Chem.*, **26**, 931 (1934)).

**Loading Agents** — Loading agents are as specialized as accelerators. The large-volume loading agent is channel-black carbon in tyres. The abrasion resistance is greatly increased when 50 parts by weight of channel black are used with 100 parts by weight of rubber. The "compounding" problem is increased when synthetic rubbers are considered.

There are four classes of carbon blacks (see same) namely, channel black, furnace black, thermal decomposition black, and lamp black. When GR-S type rubbers are used, the furnace blacks are generally used. The thermal blacks are used in either natural or synthetic compositions when resilience or high loading is desired. The lamp black is used only for colouring (Campbell, *Rubber Age*, **50**, 21 (1941)).

The inorganic loading agents are whiting, zinc oxide, lithopone, and clay. Here again the service dictates the material to be used. Titanium dioxide is used as the main loading agent for pure white stocks.

**Softeners or Plasticizers** are compounds that decrease the difficulty of processing. Mechanical working of the rubber, and the addition of petroleum oils, aromatic resins, or pine tars may be used for plasticizing. For GR-S, pine tars, aromatic resins, and petroleum products are effective, but for the butadiene-acrylonitrile type, esters such as dibutyl phthalate, dioctyl phthalate, and dibutyl sebacate are preferred.

The development of plasticizers occupies considerable time in many laboratories. H. Jones (*Trans. Inst. Rubber Ind.*, **21**, 298 (1946)) describes plasticizers as stable chemical compounds of low volatility, capable of permanent miscibility with polymers. They are believed to operate by separating the chains of the polymer and thus decreasing the effect of the intermolecular forces.

**Vulcanite, Ebonite, or Hard Rubber** is made by heating 2 parts of natural rubber and 1 part of sulphur at 150°C. Accelerators and loadings are of little or no value in the ebonite reaction. Hard rubber is widely used where resistance to chemicals and physical permanence is desirable (D. F. Twiss, *J. Soc. Chem. Ind.*, **44**, 106T (1925)). A resumé of the literature on hard rubber with pertinent information on the vulcanizing process is given by Kemp and Malm in *Ind. Eng. Chem.*, **27**, 141 (1935). The thermal-setting plastics have replaced ebonite in many cases. The synthetic hard rubbers are compared in *Ind. Eng. Chem.*, **38**, 687 (1946) in detail.

#### SOME PROPERTIES OF HARD RUBBER

Rubber-sulphur ratio	..	..	65/35
Tensile strength	..	..	800 kg./sq. cm.
Elongation at break	..	..	6.00 per cent.
Power factor	..	..	$80 \times 10^4$ at $10^6$ cycles/sec.

**Permeability** — The permeability of rubber and rubber-like substances has been carefully determined by van Amerongen (*Rev. Générale du Caoutchouc*, **21**, No. 3, 50 (1944)). The comparisons are made in Q values, which are defined as the number of cubic centimetres

of a gas at 0° C. and 760 mm. Hg pressure that passes per second through a section of rubber having a surface of 1 square centimetre, a thickness of 1 centimetre, and a difference of pressure of 1 atmosphere between the two sides of the membrane.

Elastomer						Q Value $\times 10^{-8}$
Natural rubber .. .. .	..	..	..	..	..	40
Buna-S .. .. .	..	..	..	..	..	30
Perbunan .. .. .	..	..	..	..	..	12.5
Neoprene G .. .. .	..	..	..	..	..	11.5
Neoprene E .. .. .	..	..	..	..	..	11.0
Vinyl chloride polymer .. .. .	..	..	..	..	..	8
Thiokol B .. .. .	..	..	..	..	..	1
Butyl .. .. .	..	..	..	..	..	<1

**Reclaimed Rubber** dates back to about 1900, when cracked rubber was heated with 5 to 6 per cent. alkali solution for twelve to eighteen hours at 365° to 387° F. Washing, drying, and working up with oil completes the preparation for future use. Reclaimed rubbers of various grades are obtained, and are classified according to the source. Many modifications of a compound are possible by judicious use of reclaim with resulting processing advantages (John M. Ball, *Reclaimed Rubber* (Rubber Reclaimers Assoc.); Kershaw in *Ind. Chem.*, **4**, 115 (1928); C. S. Powell in *Ind. Eng. Chem.*, **23**, 701 (1931)).

*References:* Abrasion resistance, *Trans. Inst. Rubber Ind.*, **20**, 101 (1944); *Caoutchouc and Rubber* (U.S.S.R.), **1937**, June, p. 37; *Rubber Chem. and Tech.*, **14**, 786 (1941); *Trans. Inst. Rubber Ind.*, **21**, No. 6, 375 (1946); Acceleration, *Caoutchouc and Rubber* (U.S.S.R.), **2**, 53 (1937); *Rubber Chem. and Tech.*, **11**, 97 (1938); *Trans. Inst. Rubber Ind.*, **12**, 161 (1936); Accelerated aging, *Journal of Research*, **16**, No. 2, 37 (1947); *Rubber Chem. and Tech.*, **20**, 760 (1947); Adiabatic stress-strain curves, *Monatschrift für Chemie*, **72**, 22 (1938); Anode process, *Ind. Eng. Chem.*, **25**, 609 (1933); Soft rubber vulcanization, *Ind. Eng. Chem.*, **25**, 1042 (1933); **26**, 434 (1934); Bacterial decomposition, *Ind. Eng. Chem.*, **28**, 847 (1936); Behaviour of rubber at low temperatures, *Proc. Rubber Tech. Conf.*, Paper No. 14 (1938); *Rubber Chem. and Tech.*, **12**, 344 (1939); Bonding rubber to metals, *Trans. Inst. Rubber Ind.*, **19**, 25 (1943); Brittle point of elastomers, *Ind. Eng. Chem.*, **35**, 864 (1943); **35**, 949 (1943); *India Rubber World*, **109**, 41 (1943); Cellular rubber, *Rubber Chem. and Tech.*, **17**, 943 (1944); Cements, *Ind. Eng. Chem.*, **33**, 809 (1941); Chlorinated rubber, *J. Soc. Chem. Ind.*, **57**, 327 (1938); *Ind. Eng. Chem.*, **34**, 466 (1942); Constitution and molecular weight, *Helv. Chim. Acta*, **24**, 217 (1941); Crystallization, *Trans. Faraday Soc.*, **37**, Part 2, 84 (1941); *Rubber Chem. and Tech.*, **15**, 251 (1942); Dynamic properties of rubber, *J. Applied Mechanics*, **9**, A 129 (1942); *Ind. Eng. Chem.*, **33**, 1032 (1941); *J. Sci. Instruments*, **21**, 193 (1944); **22**, 167 (1945); *Rubber Chem. and Tech.*, **18**, 470 (1945); Elasticity, *Helv. Chim. Acta*, **18**, 570 (1935); Estate Practice, *Trans. Inst. Rubber Ind.*,

9, 112 (1933); Frictional Properties, *J. Research Nat. Bur. Standards*, **28**, 439 (1942); *Rubber Chem. and Tech.*, **16**, 155 (1943); Isomerization, *Helv. Chim. Acta.*, **20**, 1393 (1937); Oxidation products, *Proc. Rubber Tech. Conference*, Paper No. 103, 1938; *Rubber Chem. and Tech.*, **12**, 225 (1939); Plastometers, Williams, *Ind. Eng. Chem.*, **26**, 345 (1934); *Rubber Chem. and Tech.*, **18**, 877 (1945); Goodrich, *Ind. Eng. Chem.*, **21**, 768 (1929); Firestone, *Physics*, **7**, 73 (1936); Mooney, *Ind. Eng. Chem. (Anal. Ed.)*, **6**, 147 (1934); Raw rubber, plastic flow, *Trans. Faraday Soc.*, **36**, Part 4, 538 (1940); *Rubber Chem. and Tech.*, **13**, 795 (1940); Isothermal stretch, *Kautschuk*, **14**, No. 5, 77 (1938); Refractive index, *J. Research Nat. Bur. Standards*, **14**, 553 (1935); Resistivity, *Trans. Inst. Rubber Ind.*, **17**, 33 (1941); Reinforcement, *Canadian Chem. and Met.*, **21**, February (1937); Scorching, *Ind. Eng. Chem.*, **20**, 1223 (1928); *Ind. Eng. Chem. (Anal. Ed.)*, **3**, 297 (1931); *Canadian J. Research*, **6**, 398 (1932); Shatter point, *Ind. Eng. Chem.*, **35**, 949 (1943); Specify gravity, *Archief voor de Rubbercultuur*, **23**, 130 (1939); *Rubber Chem. and Tech.*, **13**, 422 (1940); Spectra, *Rev. Générale du Caoutchouc*, **22**, No. 5, 103 (1945); Speed of retraction, *J. Applied Physics*, **15**, 740 (1944); Summary Reports of the Crude Rubber Committee of the Rubber Division of the American Chemical Society, *Rubber Chem. and Tech.*, **12**, 633 (1939); Swelling, *Trans. Faraday Soc.*, **38**, No. 255, 418 (1942); *Rubber Chem. and Tech.*, **16**, 263 (1943); Swelling, *Ind. Eng. Chem.*, **37**, 64 (1945); Thiorubber, *Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*, **219**, No. 16, 395 (1944); Vulcanization, *Gomma*, **1**, No. 2, 38 (1937); *Rubber Chem. and Tech.*, **10**, 725 (1937); *Rubber Chem. and Tech.*, **12**, 805, (1939); *Rev. Générale du Caoutchouc*, **18**, 289 (1941); *Rubber Chem. and Tech.*, **19**, 876 (1946); General, *Proceedings of the First and Second Rubber Technology Conference*, London, 1938 and 1948, respectively (W. Heffer and Sons, Cambridge).

**RUBBER-SEED OIL**, as extracted from the seeds of the Para rubber-tree, may possibly prove a substitute for linseed oil, but it has been shown that the seed depreciates on storage, and yields an oil containing up to 25 per cent. of free fatty acids, which is not generally suitable for that purpose. It exhibits a slower drying character than linseed oil, and it is necessary to prepare a "boiled" oil for commercial purposes which is free from fatty acids. It is stated to find a ready sale in the U.S.A. for soap manufacture. The sun-dried kernels yield about 47 per cent. oil of sp. gr. 0.925 to 0.93 at 15° C., sap. v. 188.5 to 192.5 and i.v. of 128.3 to 143.3. The residual cake is said to be a good cattle food.

**RUBIAN** — The glycoside of madder (the root of *Rubia tinctoria*), which yields alizarin and glucose by hydrolysis. (See Alizarin.)

**RUBIDIUM (Rb) and its Compounds** — Atomic weight 85.48. See Elements for other data. Rubidium is a somewhat rare element met in association with potassium and sodium in the minerals *lepidolite*, *porphyrites*, and *carnallite*. It is a soft, silvery-white metal, melting

slightly above room temperature, and, when sublimed, forms small needle-shaped crystals. It can be prepared by the electrolysis of the fused chloride, or by heating the carbonate with carbon. The mother liquor from the extraction of potassium chloride from carnallite contains the salts represented by  $\text{RbCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$  and  $\text{CsCl}, \text{MgCl}_2, 6\text{H}_2\text{O}$ , and constitutes a good source. It is capable of decomposing water, and takes fire in the air, yielding the oxide, so that, like sodium, it has to be kept under naphtha. It gives off a green vapour when heated.

Rubidium salts are soluble, resemble those of potassium in their general characters, and give a dark red colour to flame.

Compounds of rubidium resemble those of potassium; they include the **carbonate** ( $\text{Rb}_2\text{CO}_3$ ); the **chloride** ( $\text{RbCl}$ ); the **nitrate** ( $\text{RbNO}_3$ ); the four **oxides**,  $\text{Rb}_2\text{O}$ ,  $\text{Rb}_2\text{O}_2$ ,  $\text{Rb}_2\text{O}_3$ ,  $\text{Rb}_2\text{O}_4$ , all of which are yellow except  $\text{Rb}_2\text{O}_3$  which is black; the **sulphate** ( $\text{Rb}_2\text{SO}_4$ ); and many others are known.

**RUBIES** — Gems of pure clear red corundum (aluminium oxide) of great hardness. Inferior spinels are also sold as rubies. (See Aluminium.)

**RUE (OIL OF)** — The volatile oil obtained by distillation of the rue plant, *Ruta graveolens*, containing about 90 per cent. of methylonyl-ketone with a small amount of methyl anthranilate. It is viscid, of strong, unpleasant odour and bitter taste; sp. gr. 0.832 to 0.845 at  $15^\circ\text{C}$ .; opt. rot.  $0^\circ$  to  $+3^\circ$  at  $20^\circ\text{C}$ .; ref. ind. 1.430 to 1.440 at  $20^\circ\text{C}$ . (See Rutin.)

**RUM** — An alcoholic drink of characteristic odour distilled from fermented molasses in the West Indies, and ordinarily containing about 48 per cent. alcohol associated with a large amount of ethyl acetate. It is frequently coloured with caramel, and is credited as having a greater food value than any other spirit.

**RUSA GRASS** — See Ginger-Grass Oil.

**RUST** — The corrosion known as rust on iron articles is very variable in composition, and results from the chemical action of carbon dioxide and moist air, associated with, or resulting from, electrolytic action. It always contains some ferrous oxide, the proportion decreasing with age, and its formation is probably the first stage in the production of rust.

Cast iron of high impurity corrodes slowly, whereas the purest wrought iron rusts very rapidly.

Iron is said to be perfectly protected against rust by coating with certain oils, such as castor oil and wool-grease oil, which oils have been previously treated with phosphorus pentoxide in the cold or at a moderate temperature whereby a combination as phosphate takes place. In this way greases are produced, which may be used in dilute solutions, using solvents, such as benzol or alcohol, or admixed with other greases, oils, varnishes, and paints.

A surface layer of ferroferric oxide ( $\text{Fe}_3\text{O}_4$ ) or of ferric phosphate is protective against rusting. Rust does not form when iron is exposed to air-free water or water-free (dry) air. When once started, rusting

is accelerated by rust—probably by its adsorption of oxygen and moisture.

A process for the electrolytic removal of rust from iron and steel articles has been devised, using a bath containing  $\frac{3}{4}$  pound commercial caustic soda, a similar quantity of washing soda,  $\frac{1}{4}$  pound of salt cake, and 1 ounce of sodium cyanide in a gallon of water, the article to be de-rusted forming the cathode, at a temperature approximating the boiling-point.

**RUSTLESS (STAINLESS) IRON AND STEEL** — A chromium-iron alloy, containing from 12 to 16 per cent. chromium, and (for most purposes) not more than 0.35 per cent. of carbon, now largely used for the manufacture of cutlery, turbine blades, acid pumps, hydraulic pumping rams and rods, and exhaust valves for aircraft engines. In some cases a proportion of the chromium can be replaced to advantage by copper, nickel, silicon, etc. It is not attacked by any kind of water, or alkaline salts, ammonia, vinegar, fruit juices, or atmospheric agency, but ammonium chloride has some action upon it. It is also attacked by 20 per cent. acetic acid after some time, and more quickly when hot, but it is not dissolved by strong nitric acid, while sulphuric and hydrochloric acids attack it readily.

Nickel, when used in quantities of from 25 to 30 per cent., has a great effect in increasing the resistance of steel to corroding influences, and is practically used in the proportion of about 8 per cent. with 18 per cent. chromium in making some varieties.

It is important to note that "rustless" or "stainless" steel is made in many varieties adapted to particular applications, and possessed of varying properties accordingly.

Before rustless steel can exhibit resistance to the highest extent it must be heat-treated, by heating to about 940° C., and then quenching in oil. This, however, makes it too hard for some purposes, and to reduce this, it is reheated to 650° C., which treatment also improves the ductility.

The pickling bath treatment, giving the best results with mild stainless steel, is reported to consist of ten minutes' immersion in a 50 per cent. commercial hydrochloric acid, then transference without washing to 20 per cent. nitric acid for twenty-five minutes, both in the cold, the proper pickling being an important factor in its manufacture.

It is reported that articles of any metal may be rendered unstainable by the electrolytic deposition of a film of chromium. In the home and for many purposes, including construction of buildings, these various makes of so-called austenitic steels find constantly increasing employment.

It has been pointed out that the terms "stainless" and "non-corrosive" are inaccurate, since they are more accurately described as "corrosion-resistant." (See J. A. Matthews (*Ind. Eng. Chem.*, **21**, 1158 (1929)), who gives in his article a table of analyses of various types of steels on the market, including stainless steel, stainless irons, and several makes of "Rezistal"; *Stainless Iron and Steel*, by J. H. G. 30\*

## 938 RUSTLESS (STAINLESS) IRON AND STEEL — RYE-GRASS

Monypenny (Chapman and Hall, London) ; *The Book of Stainless Steels* by E. E. Thum (American Society for Metals, Cleveland, Ohio) ; *Stainless Steels*, by P. H. Miller (Oxford University Press) ; Corrosion, Iron, Metals, Paints, and Passivity.)

**RUTHENIUM (Ru) and its Compounds** — Atomic weight, 101·7. See Elements for other data. Ruthenium is a hard, brittle, greyish-black metal of the platinum group, with the ores of which it is found in association, also in the very rare mineral *laurite* as sulphide ( $\text{RuS}_2$ ). It is practically insoluble in acids other than aqua regia, and has a higher melting-point than platinum.

Ruthenium compounds consist of the following : five **oxides**,  $\text{Ru}_2\text{O}_3$ ,  $\text{RuO}_2$ ,  $\text{Ru}_4\text{O}_6$ ,  $\text{Ru}_2\text{O}_5$ , and  $\text{RuO}_4$ , all of which are black except  $\text{RuO}_4$ , which is yellow ; three **chlorides**,  $\text{RuCl}_2$ ,  $\text{RuCl}_3$ , and  $\text{RuCl}_4$ , dark coloured solids ; the **nitrate** ( $\text{Ru}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), a pale yellow, very soluble, crystalline solid ; potassium ruthenate ( $\text{K}_2\text{RuO}_4 \cdot \text{H}_2\text{O}$ ), and hexachlororuthenate ( $\text{K}_2\text{RuCl}_6$ ) ; and two carbonyls, of which the dicarbonyl is soluble in water.

**RUTHERFORD** — The standard rate of radioactive disintegrations, namely,  $10^6$  disintegrations per second.

**RUTILE** — Mineral titanium dioxide ( $\text{TiO}_2$ ), of crystal system No. 2, and sp. gr. 4·18 to 4·22, occurring in several of the U.S.A. and elsewhere. (See Titanium.)

**RUTIN (Sophorin)** ( $\text{C}_{27}\text{H}_{30}\text{O}_{16}$ ) — A substance originally discovered in rue (*Ruta graveolens*) and occurring in a number of plants, including *Viola tricolor*. It is a glycoside of pale yellow, crystalline character, sparingly soluble in water and alcohol, which upon hydrolysis yields rhamnose. The petals of *Eschscholtzia californica* are said to contain 5 per cent. of rutin. It has been found to decrease capillary fragility, and is manufactured on a commercial scale for medicinal use. (See Porter *et al.*, U.S. Dept. Agric., Bur. Agric. and Chem., A.I.C. 159, 6 (1947) ; and Rue.)

**RYE** — A genus of grasses or cereal (secale, cereale) used in making Hollands and a variety of Russian beer (" Kvass ") and from which the black bread of Germany is also made. The straw is valued for straw-plait, being tougher than that of other corn plants. (See Ergot of Rye.)

Rye oil, constituting about 2 per cent. of the rye, has been examined by J. W. Croxford (*Analyst*, 55, 735 (1930)), who found the sp. gr. as varying from 0·9374 to 0·9412 ; i.v., 118·3 to 129·9 ; and sap. v. 173·4 to 178·7 in respect of two samples. The calculated composition of the fatty acids contained in one of the oils examined was linolic, 62·65 per cent. ; oleic, 10·35 per cent. ; solid, 27·0 per cent. ; the unsaponifiable content being abnormally high. It is classified as a semi-drying oil.

**RYE-GRASS (Lolium)** — Used as forage, the perennial type being most cultivated.

**SABADILLA** (*Cevadilla*, **Caustic Barley**) — The dried ripe seeds of *Schænocaulon officinale*, from which veratrine is prepared, and which grows in Mexico, Guatemala, and Venezuela. Used as an insecticide. (See Veratrine.)

**SABINENE** ( $C_{10}H_{16}$ ) — A dicyclic terpene, isomeric with and chemically very similar to pinene, contained in savin, juniper, and marjoram oils, of b.p.  $164^{\circ}C$ . and sp. gr. 0.848. It forms a hydrochloride and a nitrosochloride. (See Savin Oil.)

**SACCHARATE** (**Strontium**) — There are two compounds of sucrose with strontia, known respectively as monostrontia monosucrose ( $C_{12}H_{22}O_{11} \cdot SrO$ ) and the distrontia compound ( $C_{12}H_{22}O_{11} \cdot 2SrO$ ). (See Sugar.)

**SACCHARIC ACID** ( $COOH(CHOH)_4COOH$ ) — A soluble, deliquescent product of the oxidation of cane sugar, glucose, starch, etc., by nitric acid.

**SACCHARIDES** — See Carbohydrates, and Sugar.

**SACCHARIFICATION** — Conversion of starch, wood, etc., into sugar. (See Alcohol, Beer, Glucose, Sugar, and Wood.)

**SACCHARIMETER** — An instrument for ascertaining the amount of sugar in a solution by determining the specific rotatory power, that is, measuring the angle through which the plane of polarized light is turned when passing through its solution in comparison with that of a solution of known strength. The term is also applied to an apparatus for measuring the volume of carbon dioxide evolved by fermentation of a definite quantity of sugar.

**SACCHARIN** ("Saxin") (**Ortho-Benzoylsulphimide**) ( $C_6H_4 \cdot CO \cdot NH \cdot SO_2$ )

— A synthetically prepared, white, crystalline substance having a sweetening power about 550 times as great as that of sugar, and used by diabetics as a sweetening agent. The standard saccharin tablets on the British market must contain 0.2 grains, with which is incorporated a little sodium bicarbonate to render the saccharin soluble in aqueous fluids; in the presence of water the acid saccharin reacts with the bicarbonate to form the sodium derivative with the evolution of carbon dioxide. "Saxin" is the proprietary brand of sodium saccharin, each tablet containing 0.25 grains. Saccharin is excreted unchanged in the urine and is quite harmless, even in large doses taken for years. (See "A Treatise on Saccharin: Its Laboratory and Industrial Preparation" (*Afinadid*, Spain, 23, 321 (1946)).)

**SACCHAROMETER** — Hydrometer graduated to test the strength of sugar solutions by ascertaining their density, and reference to Tables prepared from known strengths.

The Brix hydrometer and the Balling saccharometer are graduated so that the number of degrees is identical with the weight per cent. of sucrose when used at the temperature of calibration.

**SACCHAROSES** (**Saccharides**) — See Carbohydrates, and Sugar.

**SAFETY GLASS** — See Glass.

**SAFETY** — Concerning "Employee Safety Through Building Design," the Handling and Storing of Materials, Ventilation and Air-Conditioning, and Illumination, see *Ind. Eng. Chem.*, **29**, 609 (1937), by E. R. Grannis of the National Safety Council, Chicago. Also see Antidotes, Hazardous Chemicals, Lead, Poisons, and Silicosis.

**SAFFLOWER** — The dried florets of *Carthamus tinctorius* (Fam. Compositæ), a herbaceous plant cultivated in India. It contains a red colouring matter, carthamin, and is used as a dyestuff for cotton goods without a mordant. The seeds contain from 14 to 30 per cent. of fixed oil consisting of the glycerides of isolinolenic, linoleic, oleic, palmitic, and stearic acids.

The oil has drying properties and can be used in varnish-making and for making soap. Dried to a gelatinous mass, safflower oil is used as "Roghan" or "Afridi" wax in preparing wax cloth. The "sweet oil" of Bombay is a mixture of oils expressed from safflower, earth nut, and *til* seeds.

**SAFFRON** — The dried stigmas of *Crocus sativus*, cultivated in Spain, France, Austria, and Italy. It has been used as a dyestuff and as a flavouring agent but is rarely seen in commerce. It contains a yellow colouring matter, crocin, and a crystalline bitter glycoside, picrocrocin.

**SAFRANINES** — A group of diaminoazines containing at least three hydrocarbon nuclei, strongly basic crystalline compounds, readily soluble in water, and dyeing yellowish-red to violet colours. The first aniline dye to be made, namely, mauve, is a mixture of phenylated safranine. Phenosafranine is the simplest member of the group.

**SAFROLE** ( $C_{10}H_{10}O_2$ ) — The essential constituent of sassafras oil from the bark of *Sassafras officinalis* of N. America; contained also in losoh oil (from the wood of *Cinnamomum parthenoxylon* of the Malay States), camphor wood, and other plants. It is clear, colourless, of sp. gr. 1.10, m.p. 11° C., and b.p. 234° C.; soluble in alcohol and ether, of aromatic odour, and upon cooling to -20° C. crystallizes in rhombic prisms; used in perfumery and, by oxidation with chromic acid, yields heliotropin. (See Sassafras Oil.)

**SAGE (OIL OF)** — An essential oil distilled (about 1.5 per cent.) from the fresh leaves of *Salvia officinalis*, a genus of Labiatae, growing in north Mediterranean countries, containing sesquiterpenes, cineol, borneol, etc. Sp. gr., 0.910 to 0.930; opt. rot., +10° to +25° at 20° C.; ref. ind., 1.462 to 1.467 at 20° C.; used in perfumery and making condiments. The composition of oil obtained from *Salvia sclavea* is given by G. Rovesti in *Italia Agric.*, **83**, (2), 105 (1946).

**SAGGARS** — Cases of baked fire-clay in which certain classes of pottery and porcelain are fired to protect them from the direct heat.

**SAGO** — Consists almost entirely of starch, and is prepared in the islands of the Indian Archipelago from the pith of the stems of certain palms, including the *Sagus* (*Metroxylon rumphii* W., *S. raffia* Jacq., *S. lavis*,

etc., which grow freely in Java, the Moluccas, Borneo, Siam, New Guinea, Sumatra, and elsewhere. Each tree is stated to yield about 600 pounds of pith. (See Cassava, and Tapioca.)

**SAJJI** — See Ritha.

**SAKI (Saké)** — A beer made by the Japanese from rice by a process of fermentation induced by a mycelium named *koji*, which grows on steamed rice. This and various species of aspergillus are known to produce, under suitable conditions, kojic acid ( $C_6H_6O_4$ ) from rice, sugar, glycerol, etc., and this acid, which is closely related to glucose, has been synthesized.

**SAKOA OIL**, from Madagascar, is obtained from the fruit of *Sclerocarpa caffra*. The seeds contain 56 per cent. of a non-drying oil, having a sp. gr. at 15° C. of 0.9167, sap. v. 193.5, and i.v. 76.6.

**SAL AMMONIAC** — An old name for ammonium chloride marketed as "sublimed lump," first and second qualities.

**SAL VOLATILE** — See Nitrogen (Ammonium Carbonate).

**SALICIN** ( $C_{13}H_{18}O_7$ ) — A colourless, odourless, crystalline glycoside obtained from the bark of various species of *Salix* and *Populus*; soluble in water and alcohol; insoluble in chloroform and ether; m.p. 199° to 201° C. It is seldom used in medicine but has been employed for the treatment of rheumatism. (See Saligenin.)

**SALICYLANILIDE** ( $C_6H_4(OH).CO.NH.C_6H_5$ ) — A white powder incorporated into the warp size to protect cotton cloths from mildew effects. It has also been used in medicine for the treatment of fungal infections such as ringworm of the scalp (see L. Schwartz, *J. Amer. Med. Ass.*, **132**, 58 (1946)), and R. T. Brain, K. Crow, H. Haber, C. McKenny, and J. W. Hadgraft, *Brit. Med. J.*, **1**, 724 (1948)). Trade-mark is "Shirlan" (Du Pont).

**SALICYLIC ACID (Ortho-Hydroxybenzoic Acid)** ( $C_6H_4(OH)COOH$  (1, 2)) occurs naturally in the blossom of *Spiræa ulmaria* and in combination in oil of wintergreen. It is a white, crystalline body, of m.p. 159° C., prepared by the action of carbon dioxide at 130° C. upon sodium phenoxide (phenate) ( $C_6H_5ONa$ ) in a closed vessel, the sodium phenyl carbonate thus produced being subsequently transformed into sodium salicylate, and from it the acid is obtained by the action of sulphuric or hydrochloric acid. It can also be easily obtained by chemical methods from salicin, coumarin, phenol, oil of wintergreen, and indigotin. It is little soluble in cold water, but readily soluble in alcohol, ether, and hot water; is a good antiseptic, and is much used in the dyestuffs industry and the manufacture of aspirin; also medicinally and as a preservative agent by glue-makers and for foods and skins. For internal administration medicinally, it is used as the sodium salt.

**SALICYLIC ALDEHYDE (Ortho-Hydroxybenzaldehyde)** ( $C_6H_4(OH)CHO$  (1, 2)) — A yellow oily substance of sp. gr. about 1.167, m.p. 1.6° C., b.p. 196.5° C., soluble in alcohol and ether, and prepared by interaction of phenol and chloroform in presence of potassium hydroxide. Used in perfumery.

**SALIGENIN (Ortho-Hydroxybenzyl Alcohol)** ( $C_6H_4(OH)CH_2OH$  (1, 2)) — A crystalline product, of m.p.  $86^\circ C.$ , obtained in equimolecular proportions with glucose upon hydrolysis of the glycoside salicin ( $C_{13}H_{18}O_7$ ).

**SALINOMETERS** — Hydrometers for ascertaining saline density of water, as for ships' boilers.

**SALIVA** — An alkaline mixture of fluids secreted by various salivary glands (the ducts of which discharge into the mouth) containing an active principle termed ptyalin which behaves as an enzyme and converts starchy matters into sugar (maltose). It contains about  $1\frac{1}{2}$  parts ptyalin per 1,000, and is most active at  $40^\circ C.$

**SALMON OIL** — See Fish Oils.

**SALOL** — See Phenyl Salicylate.

**SALSOLA** — A genus of seashore plants, rich in salts, which, when burned yield an ash containing sodium carbonate. (See Barilla, and Kelp.)

**SALT (Common)** — See Sodium (Chloride).

**SALT CAKE** — Crude sodium sulphate from the manufacture of hydrochloric acid from sodium chloride and sulphuric acid.

**SALT OF LEMON** — See Potassium (Binoxalate).

**SALT OF SORREL (Salt of Lemon)** — See Potassium (Binoxalate).

**SALTPETRE, CHILE** — See Caliche.

**SALTPETRE (Nitre)** -- See Potassium (Nitrate).

**SALTS** — See Acids, Chemical Compounds, and the Metals concerned.

"**SALVARSAN**" — See Arsphenamine.

**SALVIA** — See Sage Oil.

"**SALYRGAN**" — See Mersalyl.

**SAMARIUM (Sm) and Its Compounds** — Atomic weight, 150.43. See Elements for other data. Samarium is a member of the rare-earth group of elements and belongs to the cerium group of the same, and occurs in samarskite and some other rare minerals.

The salts of samarium are yellowish, and include the **chloride** ( $SaCl_3 \cdot 6H_2O$ ), and the **bromide** ( $SaBr_3 \cdot 6H_2O$ ). The **oxide** is  $Sa_2O_3$ , a yellow solid.

**SAMARSKITE** — A complex yttrium mineral found in North Carolina and near Miask in the Ilmen Mountains, containing cerium, columbium, samarium, tantalum, uranium, yttrium, etc.; crystal system No. 4, and sp. gr. about 5.6. Hess and Wells have concluded from their analyses that this mineral consists of two compounds of formulas approximately  $Y_2O_3 \cdot Cb_2O_5$  and  $2Y_2O_3 \cdot 3Cb_2O_5$ .

**SAND** — Granular, hard, siliceous material, being disintegrated rock in pulverulent form. There are various sands used for industrial purposes, including abrasive sands, bevelling sands, a kind used for casting aluminium and steel, another for use in making asphaltic paving;

sands for copper, brass, and bronze moulding ; carborundum sands for building and filtration purposes. Some kinds consist almost entirely of silica, and are used in glass-making, the manufacture of porcelain and other wares, etc. (See Glass, and Silica.)

**SANDAL WOOD (Santal Wood)** — The heartwood of *Santalum album*, a small tree growing in Southern India, Mysore, and Madras, used for the distillation of a volatile oil. Sandal-wood oil contains up to 90 per cent. of santalol, a mixture of two isomeric sesquiterpene alcohols having the molecular formula  $C_{15}H_{24}O$  ; it also contains small amounts of santalyl acetate and an aldehyde, santalal,  $C_{15}H_{22}O$  ; sp. gr. 0.973 to 0.985 at 15° C. ; opt. rot.  $-15^{\circ}$  to  $-20^{\circ}$  at 20° C. ; ref. ind. 1.500 to 1.510 at 20° C. Sandal-wood oils are used in perfumery but seldom in medicine.

**Australian Sandal-Wood Oil** — The volatile oil distilled from the wood of *Santalum spicatum* (*Eucarya spicata*), a bush growing in West Australia. Australian sandal-wood oil contains 90 to 95 per cent. of alcohols which are isomeric with santalol ; sp. gr. 0.970 to 0.976 at 15° C. ; opt. rot.  $-3^{\circ}$  to  $-10^{\circ}$  at 20° C. ; ref. ind. 1.498 to 1.508 at 20° C., soluble in alcohol, ether, and carbon disulphide.

**Red Sanderswood** — The wood of *Pterocarpus santalinus*, a tree growing in Southern India and the Philippine Islands, sometimes called red sandal wood. It contains santalin, a red colouring matter, obtained in fine red crystals, insoluble in water but soluble in alcohol. Red sanderswood is used in India for dyeing cotton and silk, to which it imparts red colours of various hues.

**SANDARAC** — See Gums and Resins.

**SANDSTONES** — Compacted siliceous stones, more or less ferruginous in character, used for building purposes. Sandstone can be converted into a much more concrete and hard condition by impregnation with sulphur. (See Sand, and Sulphur.)

**SANITATION** — See Hygiene.

**SANTALIN** — See Barwood, and Sandal Wood.

**"SANTICIZER"** (1, 2, 3, 8, 9, B-16, E-15, M-17) — A series of proprietary plasticizers for use in making cellulose lacquers.

**SANTONIN** ( $C_{15}H_{18}O_3$ ) — A colourless, crystalline lactone, obtained from the unexpanded flowerheads of *Artemisia cina* and other species of *Artemisia* growing in Cashmere, Mexico, Russia, and Western Tibet ; insoluble in water ; soluble in alcohol and chloroform ; m.p. 171° to 174° C. The drug is imported under the name of santonica and contains from 2 to 3.5 per cent. of santonin, which rapidly diminishes after the flowerheads have expanded. Santonin is used in medicine for the expulsion of ascarides (round-worms) and lumbricoids ; it is not effective against the tape or thread worm.

**SAPOGENINS** — The sugar-free hydrolytic products of the saponins. (See Saponins.)

**SAPONIFICATION** — A term used to express the hydrolysis of esters by alkalis, and particularly applied to the hydrolytic action whereby fats and oils containing glycerides are converted into soaps. The process is believed to take place in three stages, passing from the original triglyceride through diglyceride to the monoglyceride stage, and ultimately to completion. Magnesia is said to be the most effective base in the cases of tallow, palm-kernel oils, and whale oils; while lime is superior in the case of palm oil, and both equal in respect of linseed oil. (See Esters, Fats, and Soaps.)

**SAPONIFICATION EQUIVALENT** — See Fats (Tests).

**SAPONIFICATION VALUES (Numbers)** — See Fats.

**SAPONINS** — Plant glycosides forming, with water, colloidal solutions that froth copiously, and yielding on hydrolysis sugars and sapogenins. All of them hæmolyse red blood-corpuscles and therefore highly toxic. Chemically they fall into two groups: (1) the triterpenoid saponins, such as those occurring in the soap-barks; the sapogenins of these are believed to contain five homocyclic carbon rings in the molecule, but their structures have not yet been fully investigated, and (2) the steroid saponins, occurring, with the cardiac glycosides, in the leaves of certain species of digitalis and the bulbs of squill. The steroid saponins have been more fully investigated than the first group, and the structures of the genins, as well as the other hydrolytic products, of the following are known. (See *Natural Products Related to Phenanthrene*, by Fieser and Fieser (Reinhold Publishing Corp., New York).)

Saponin	Hydrolytic Products	
Gitonin, $C_{50}H_{82}O_{23}$	Gitogenin, $C_{27}H_{44}O_4$ (1 mol.)	Galactose (3 mol.) Pentose (1 mol.)
Tigonin, $C_{56}H_{92}O_{27}$	Tigogenin, $C_{27}H_{44}O_3$ (1 mol.)	Glucose (2 mol.) Galactose (2 mol.) Xylose (1 mol.)
Digitonin, $C_{56}H_{92}O_{29}$	Digitogenin, $C_{27}H_{44}O_5$ (1 mol.)	Galactose (4 mol.) Xylose (1 mol.)

Commercial saponin is made by extracting powdered soap bark (*Quillaia saponaria*) with hot alcohol, when the saponin crystallizes out on cooling, or by boiling the powdered dry aqueous extract with alcohol. It is used as a foam producer for beverages, as a wetting and spreading agent for garden sprays, and in sizing and fire-extinguishing. Other sources of commercial saponin are panama wood, soapberry, liquorice, etc. In the family Caryophyllaceæ saponins are very widely distributed.

**SAPPAN WOOD** — A hard, red compact wood obtained from the heart-wood of *Casalpinia Sappan* (Fam. Leguminosæ), a tree indigenous to India and grown in China, Japan, and Siam. It is known commercially as brasill or brasilly and has been used medicinally in India as an astringent.

**SAPPHIRE** ( $\text{Al}_2\text{O}_3$ ) (crystal system No. 3, and sp. gr. 4.0) — Blue gems of pure corundum ranking next to the diamond in value, found in Bohemia, Saxony, Ceylon, Cashmere, and Burmah. (See Aluminium.)

**SAPROPHYTES** — Minute organisms, including yeast cells and various bacteria, capable of inducing processes of fermentation. (See Bacteria, and Yeasts.)

**SARCINE** (Hypoxanthine) ( $\text{C}_5\text{H}_4\text{ON}_4$ ) — A weak basic body slightly soluble in water, occurring in muscular flesh and nearly related to xanthine ( $\text{C}_5\text{H}_4\text{O}_2\text{N}_4$ ). Both are chemically related to uric acid.

**SARCOSINE** (Methylglycocoll) ( $(\text{CH}_3)\text{HN}.\text{CH}_2.\text{COOH}$ ) — A weak base obtained, together with urea, by the action of baryta water on creatine :  $\text{C}_4\text{H}_9\text{O}_2\text{N}_3.\text{H}_2\text{O} = \text{C}_3\text{H}_7\text{O}_2\text{N} + \text{CO}(\text{NH}_2)_2$  (urea).

**SARDINE OIL** — See Fish Oils.

**SARDONYX** — A kind of chalcedony. (See Chalcedony.)

**SARSAPARILLA ROOT** — The dried root and rootlets of *Smilax ornata* (Jamaica sarsaparilla) and *S. medica* (Mexican sarsaparilla) (Fam. Liliaceæ). It contains a crystalline glycoside, sarsapaponin, together with mucilage and starch. An aqueous decoction of sarsaparilla is used as a soft drink in the U.S.A.

**SASSAFRAS OIL** — A yellowish volatile oil distilled (2.6 per cent.) from the root and root bark of various species of *Sassafras*, found widely distributed in Canada and N. America ; sp. gr. 1.070 to 1.084 at  $15^\circ\text{C}$ ., opt. rot.  $+1^\circ$  to  $+4^\circ$  at  $20^\circ\text{C}$ ., and ref. ind. 1.523 to 1.531 at  $20^\circ\text{C}$ . It is soluble in alcohol and ether, contains 80 to 90 per cent. safrole, together with some eugenol, pinene, and phellandrene ; used in perfumery and in the manufacture of heliotropin and piperonal. (See Safrole.)

**SATIN SPAR** — A fibrous form of gypsum (calcium sulphate).

**SATIN WHITES** — Calcium sulphoaluminates used in the paper industry.

**SATURATED COMPOUNDS** — See Valencies.

**SATURATION** — See Crystals, and Solution.

**SAVIN OIL** — A nearly colourless volatile oil, distilled from the fresh leaves and twigs of *Juniperus Sabina*, growing in Canada, Northern Europe, Asia, and America. It contains an alcohol, sabinol ( $\text{C}_{10}\text{H}_{15}\text{OH}$ ), together with cadinene and pinene ; soluble in alcohol and ether ; sp. gr. 0.905 to 0.930 at  $15^\circ\text{C}$ .; opt. rot.  $+43^\circ$  to  $+66^\circ$  at  $20^\circ\text{C}$ . ; ref. ind. 1.470 to 1.478 at  $20^\circ\text{C}$ . Savin oil was formerly used in medicine, but it is no longer commercially available in Great Britain.

**SAWDUST** is utilized, apart from its value as a packing material and fuel, in the manufacture of solvents, cellulose, paper, industrial alcohol, oxalic acid, carbon black. (See Briquetting, "Ketol," and Solvents.)

"**SAXIN**" — See Saccharin.

**SCAMMONY** — See Gums and Resins.

**SCANDIUM (Sc) and its Compounds** — Atomic weight, 45.10. See Elements for other data. Scandium, although strictly speaking it is not one of the rare-earth elements, is frequently spoken of as belonging to the cerium group of the same, on account of the similarity of the reactions of scandium and the cerium group. Scandium occurs in a few uncommon minerals, for example, *wolframite*, sometimes to the extent of 2 per cent. content of scandium oxide, *wiikite*, and *thortveitite*.

Scandium is trivalent, and forms the **oxide** ( $\text{Sc}_2\text{O}_3$ ), insoluble; the **chloride** ( $\text{ScCl}_3$ ), soluble; the **bromide** ( $\text{ScBr}_3$ ), soluble; the **nitrate** ( $\text{Sc}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ ), soluble; and the **sulphate** ( $\text{Sc}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ ), soluble; all of which are white or colourless.

**SCAPOLITES** — Natural silicates of aluminium and calcium of crystal system No. 2, and sp. gr. about 2.6.

**SCHAEFFER'S ACID** — 2-Naphthol-6-sulphonic acid.

**SCHALLERITE** — A brown mineral described as of volatile character and composition  $12\text{MnO}, 9\text{SiO}_2, \text{As}_2\text{O}_5, 7\text{H}_2\text{O}$ , alleged to occur in zinc-ore veins in New Jersey.

**SCHÉELE'S GREEN** — See Copper (Compounds).

**SHEELITE** — See Tungsten.

**SCHISTS** — Crystalline rocks of foliated structure, such as mica-schist and hornblende-schist; the term is also applied to indurated clay-rocks. (See Shale, and Petroleum.)

**SCHLIPPE'S SALT** ( $\text{Na}_3\text{SbS}_4 \cdot 9\text{H}_2\text{O}$ ) — Sodium thioantimonate (from which so-called "golden sulphide" (as used in colouring vulcanized rubber goods) is made by decomposing it with dilute sulphuric acid). It is prepared by fusing antimony ore (sulphide) with dry sodium sulphate, charcoal, and sulphur, and concentrating the aqueous extract thereof to the point of crystallization.

**SCHÖNITE** — A double sulphate of magnesium and potassium found among the Stassfurt deposits.

**SCHWEINFURT GREEN (Paris Green)** — See Copper (Compounds).

"**SLERON**" — An aluminium alloy resembling "Duralumin," but containing lithium partially or entirely in place of magnesium.

**SLEROPROTEINS** — Insoluble proteins, being constituents of the skeletal parts of certain tissues such as cartilages, ligaments, hoofs, nails, hair, sponge, coral, etc.

**SCOPOLAMINE** — See Hyoscine Hydrobromide.

**SCOURING** — Recognized phases of scouring are: (1) solvent scouring, depending upon the extraction of oily and fatty matters from fibres and fabrics by direct solvent action of benzene, petrol, chlorinated hydrocarbons, etc.; (2) saponification, by conversion of fatty matters into soaps by action of alkali, and removal of these soluble products by

solution ; (3) emulsification, by which greasy dirt is removed mechanically, the frothy lather or emulsion being wetted out ; (4) attrition or mechanical scouring by fuller's earth, etc.

**SCREENING** — See Separation.

**" SCRIM OIL "** — Linoxyn as made in the Walton process of linoleum manufacture.

**SCRUBBING** — See Gas Absorption, and Gas Washing.

**" SCUROFORM "** — See Butyl Aminobenzoate.

**" S-D-O "** — When acetylene is passed into an aqueous solution of cuprous chloride and ammonium chloride, two principal reactions take place. When monovinylacetylene is the product it goes to make synthetic rubber, but when divinylacetylene is the product it is then polymerized by heating to form a synthetic drying oil, the trade name for which when dissolved in naphtha is " S-D-O." It is resistant to acids, alkalis, and solvents, and may be applied to metals, concrete, and wood.

**SEA-FOAM** — See Meerschaum.

**SEA-WATER** — See Water.

**SEA-WEEDS** — There are many species and abundant quantities, some of which are of considerable interest from a chemical point of view. Some kinds are burned for the sake of their alkaline ash, and as a source of bromine and iodine ; others being used as articles of food and as fertilizing agents on account of the high percentage of nitrogen they contain. The amount of ash varies from 17·7 per cent. in *Fucus sercatus* to 52·37 per cent. in the roots of *Laminaria hyperboria*.

*Laminaria saccharina* contains mannite, and is largely used as food in China and Japan. *Varec* or *vraic* is greatly appreciated in the Channel Islands as a valuable fertilizer, and *duftweed* is extensively used in Ireland as a dressing for potatoes. *Rhodymenia palmata* (dulse) and *Alaria esculenta* (murlins) are both used as food in the Scottish Highlands and Ireland. *Chondrus crispus* and *C. mamillosus* of the order Florideæ (carrageen, or Irish moss) contain nearly 80 per cent. of a peculiar gelatinous substance named " caregeenin," and some 70 per cent. (on the dry weight) is soluble in water. It serves as a substitute for tragacanth for certain purposes ; finds some use as food ; is used by painters instead of size ; also for making jellies, lozenges, and mucilage ; for dressing the warp of webs, for clarifying beer, and for leather dressing. The gelatinizing property is lost by treatment with mild acid hydrolysis. *Gracilaria lichenoides* (Ceylon or edible moss) is found in the Indian Archipelago and China, and, together with *Encheuma spinosum*, is used for the preparation of nutrient jelly in bacteriological research, also for gumming silks, paper, etc., and for making soups.

The protein content of sea-weeds (calculated on the dry matter) varies from 9·28 in *Chondrus crispus* to 29·06 per cent. in *Porphyra laciniata*, and the nitrogen content from 1·485 to 4·65 per cent.

Nutritive jellies can be made from several varieties of sea-weed, and a material prepared from them is used to some extent as a substitute for horn, shell, whalebone, etc. A crystalline sugar named *floridose* is obtained as a hydrolytic product from the mucilaginous substance formed by boiling sea-weeds in water. Sea-weeds are also the source of a binding material for use in briquette making known as the "Thornley Patent Binder." Bladder-wrack (*Fucus vesiculosus*) is used as a remedy for obesity and kidney trouble. (See Algæ, Algin, Iodine, and Kelp.)

**SEA-WOLF LIVER OIL** — See Fish Oils.

**SEAL OIL** — See Fish Oils.

**SEALING WAX** — A mixture made by heating together shellac, Venice turpentine, and vermilion (mercuric sulphide); another mixture is that of beeswax and resin. Resin (colophony) is often substituted in part for shellac, and various mineral colouring matters are used in place of vermilion according to the desired colour; for white sealing waxes basic nitrate of bismuth is used, giving a product of a beautiful white enamel-like brilliancy.

**SECRETIN** — A gland product which stimulates the pancreas and is concerned in the complex process of digestion.

**SEDIMENTATION** — The separation of solid particles of different sizes or densities by taking advantage of their different settling rates in a liquid medium. In the *Spitzkasten*, a suspension of finely ground ore in water is passed through a series of tanks of gradually increasing cross-section, the fluid velocity being thus progressively reduced. Larger particles are deposited in the smaller tanks and *vice versa*. Each tank has a pyramidal bottom from which the sediment is discharged. The *Dorr Thickener* has mechanical rakes which continuously remove the sediment from the bottom of a large cylindrical settling tank. In the *Wilfley Table* a suspension of fine particles in water is passed over an inclined shaking table having a grooved or riffled surface. Heavier particles settle in the grooves while the lighter particles are carried away with the water.

The principle involved in sedimentation is the application of Stokes' law of the rate of fall of a spherical body through a fluid under the influence of gravity ( $g$ ), and is expressed mathematically thus :

$$V = \frac{2g}{9} \cdot \frac{r^2}{\eta} \cdot (d_2 - d_1),$$

where  $V$  = rate of fall of particle,  $r$  = radius of particle,  $\eta$  = viscosity of the fluid,  $d_2$  = density of particle,  $d_1$  = density of fluid.

**SEED DISINFECTANTS** — See "Arasan," "Ceresan," and "Semesan."

**SELENIDES** — Compounds of selenium analogous to sulphides found in mineral forms as *benzelianite* or copper selenide ( $\text{Cu}_2\text{Se}_3$ ); *clausthalite* or lead selenide ( $\text{PbSe}$ ); and *naumannite* or silver selenide ( $\text{Ag}_2\text{Se}$ ). (See Selenium.)

**SELENITE** — See Calcium (Sulphate).

**SELENIUM (Se) and its Compounds** — Atomic weight, 78.96. See Elements for other data. Selenium resembles sulphur in its general properties. It is found in association therewith in volcanic areas in its free state ; also as selenide of sulphur in Swedish pyrites, and in combination with other metals in a number of minerals, including some copper pyrites. (See Selenides.) Russian selenium has a high reputation for purity, deliveries being found of 99.75 per cent. purity in black amorphous lump form. It is recovered to some extent in the electrolytic refining of copper from the mud that settles in the cells, also from the deposit that is thrown down from sulphuric acid in the chambers and Glover tower, and from the flues of pyrites burners.

Like sulphur, selenium is allotropic, and the following forms are recognized : (1) vitreous red selenium, of sp. gr. 4.26, obtained by precipitation ; (2) crystalline red selenium, of sp. gr. 4.46, that separates in monoclinic crystals from solutions of selenium in carbon disulphide ; (3) crystalline grey selenium A, formed by heating selenium to 175° C., and it is gradually changed into selenium B ; (4) metallic grey selenium B, of sp. gr. 4.79, insoluble in carbon disulphide, produced when the other forms of selenium are maintained at 200° C., of metallic lustre, malleable, and a conductor of electricity in proportion to the light incident upon it. The heat of transformation of the vitreous variety to the metallic form has been given at 130° C. as 13.5 calories per gram. When heated in the air, selenium burns with a blue flame, forming an oxide and emitting an offensive, pungent odour.

Selenium is used in wireless telephony, electrical and physical contrivances, in photometry, and as a decolourizing agent in the production of colourless glass, 1 part per 42,000 of glass or 0.0024 per cent. being generally added. Advantage is also taken of its peculiar electrical conductivity when exposed to light in the construction of an instrument termed the "optophone," by means of which the blind can read books through the agency of the telephone. It has been found that selenium can be economically used to flame-proof electric wire, but the quantity required for treating paper, scenery, and other diffuse materials is relatively large. Selenium has found wide uses as an alloying addition to stainless steels, copper alloys, and the low-expansion alloy "Invar" because it develops free machining qualities without impairing the resistance to corrosion. It has proved to be an important ingredient in antifouling paint for ship bottoms, in lubricating oils, and in vulcanizing synthetic rubber. (See *Strategic Minerals*, by J. B. DeMille (McGraw-Hill Book Co., New York) ; *Rarer Metals*, by Jack De Ment and H. C. Dake (Chemical Publishing Co., Brooklyn).)

The presence of selenium in some arid soils has attracted attention as a hazard to stock grazing in the region. In a dry diet it has been shown that the presence of 4 parts per million of selenium is definitely injurious. In its publications, namely Circular 320 (1934), Technical Bulletins 530, 534 (1936), the United States Department of Agriculture has made public the information acquired in their investigations, and a member of the staff, Dr. H. G. Byers, was sent to Mexico for further study of this problem. His report appears in *Ind. Eng. Chem.*, 29, 1200

(1937). Also, concerning selenium in Hawaii, see *Ind. Eng. Chem.*, **28**, 821 (1936). The selenium content of wheat from various parts of the world is reported, in parts per million, by W. O. Robinson (*Ind. Eng. Chem.*, **28**, 736 (1936)) as follows: New South Wales 0.1–0.7, Argentina 0.4–0.6, Saskatchewan, Canada, 1.9, Mexico 0.6, South Africa 0.2–1.5, Spain 0.2–0.8, Hungary 0.3–0.4, New Zealand 0.4, North Dakota 0.3, Maryland 0.1–0.2.

Two **oxides** are known, namely, the dioxide ( $\text{SeO}_2$ ), a white crystalline body which can be sublimated, and dissolves in water to form selenious acid ( $\text{H}_2\text{SeO}_3$ ) corresponding to sulphurous acid; and the trioxide ( $\text{SeO}_3$ ), obtained by the action of ozone on the oxychloride saturated with selenium. The latter is a yellow amorphous substance which decomposes at about  $120^\circ\text{C}$ . without melting, and is soluble in water and alcohol. Selenic acid ( $\text{H}_2\text{SeO}_4$ ) corresponds to sulphuric acid. Both selenious and selenic acids can be obtained in crystalline form.

Two **chlorides** are known, namely, the monochloride ( $\text{Se}_2\text{Cl}_2$ ), a brown oily compound which has the property of dissolving metallic selenium, and is slowly decomposed by water; and the tetrachloride ( $\text{SeCl}_4$ ), a pale yellow crystalline volatile substance. There are also two corresponding **fluorides**.

**Hydrogen selenide** ( $\text{H}_2\text{Se}$ ) is a colourless gas resembling hydrogen sulphide in its odour and chemical properties, obtained by the action of an acid upon a selenide, as, for example, the action of hydrochloric acid upon magnesium selenide.

**Selenium oxychloride** ( $\text{SeOCl}_2$ ) is a nearly colourless liquid, of b.p.  $176.4^\circ\text{C}$ . at 726 mm., and m.p.  $8.5^\circ\text{C}$ . It is a highly corrosive liquid, which readily dissolves selenium, sulphur, and tellurium. A claim has been made to the effect that the addition of very small quantities of selenium oxychloride (in common with diethyl telluride) to low-grade petrol prevents the "knocking" of internal combustion engines working at high compression.

The compounds of selenium and tellurium resemble each other, respectively, and are in general very toxic.

**"SEMESAN"** (Du Pont) — Trade-mark for a seed disinfectant based on hydroxymercurichlorophenol. Used in the treatment of vegetable and flower seeds, bulbs, tubers, corms, and roots.

**SEMI-** — A prefix indicative of partly or one-half. Semi-permeable membrane is one that is permeable to one substance and not to another.

**"SEMI-STEEL," S.P.M.** — A material possessing mechanical properties intermediate between those of cast iron and cast steel, of which filter-press plates and some autoclaves are constructed.

**SEMOLINA** — A farinaceous food preparation made from the hard-grain wheats of Italy, Spain, and South Russia, containing a relatively large amount of nitrogenous material.

**SENEGA ROOT** — The dried root of *Polygala Senega*, a herbaceous plant indigenous to North America and Southern Canada. It contains

senegin and polygalic acid, which are glycosidal saponins and have an irritant action on mucous membranes. Senega is used in medicine in the form of an infusion as a constituent of expectorant cough mixtures.

**SENEGAL GUM** — See Gums and Resins.

**SENNA FRUIT** — The dried ripe fruits of *Cassia acutifolia* (Alexandrian senna pods) and of *Cassia angustifolia* (Tinnevely senna pods). It contains various derivatives of anthraquinone and is used for the preparation of an aqueous infusion used as a laxative.

**SENNA LEAF** — The dried leaves of *Cassia acutifolia* (Alexandrian senna leaf) and of *Cassia angustifolia* (Tinnevely senna leaf), containing anthraquinone derivatives and used in medicine as a constituent of compound liquorice powder.

**“SENSITOL” (Green and Red)** — Two substances of dyestuff character used in the production of panchromatic photographs.

**SEPARATION** — Implies the various means of separating solids from solids, solids from liquids, and immiscible liquids (using in this case separators of a centrifugal character). Engineering appliances such as vibrating screens are used for separating the various particles of dry powders, etc. There are other contrivances such as the “Sturtevant Air-Separator,” which picks out the particles of a certain size and allows those larger to drop through, the actual size separated being determined by the speed at which the air current passes through the falling material. There are also various types of sieves, rotary screens, magnetic separators, centrifugal separators, etc. Laboratory sieves are identified by the number of meshes per linear inch, for example, U.S. Standard 60-mesh sieve has wire 0.0064 inch diameter and opening 0.0098 inch, 100-mesh 0.0042 and 0.0058 and 200-mesh 0.0021 and 0.0029, respectively. The B.S.I. (B.E.S.A.) has issued a specification for test sieves.

In industry the principal screening devices are the revolving cylindrical screen or trommel and flat vibrating screens actuated either mechanically or electrically. Flat screens make a more efficient use of the screening medium, since the whole surface is continuously in use. Industrial screens may be made of punched sheet metal for very coarse sizes, woven wire in coarse to fine meshes, bolting cloth for very fine materials such as pigments. (See *Screening and Grading*, by J. E. Lister (E. Benn, London); *Clays, Decantation, Distillation, Elutriation, Extraction, Filtration, Gas Absorption, Sedimentation, and Separation*.)

**SEPIA** — See Cuttle Fish.

**SEPIOLITE** — See Meerschaum.

**SEPTARIA** — Nodules of ironstone or argillaceous limestone, consisting mainly of calcium carbonate in admixture with silica and alumina, used in making Roman cement. (See Cement.)

**SEPTIC POISONS** — Toxic chemical products, produced by bacteria, and causing the condition known as septicæmia when introduced into the

blood-stream. A large variety of substances have this property, from proteins of large molecular weight to simple amines such as the ptomaines. When the whole blood-stream is infected the condition is known as general septicæmia, and before the advent of the sulphonamide drugs was usually fatal. (See Bacteria, Ptomaines, Pus, and Putrefaction.)

**SERALBUMIN** — Serum albumin. (See Albumins, Blood, Blood Albumin, Proteins, and Serum.)

**SERICIN** — See Silk.

**" SEROGAN "** — See Gonadotrophin.

**SERPENTINE** — Mineral forms of hydrated magnesium silicate. Some varieties contain alumina and others iron (crystal system No. 4). The formula  $H_2Mg_3Si_2O_8$  fairly represents the composition of many varieties. When heated to  $500^\circ$  to  $700^\circ$  C. it loses most of its water, and the crystal structure becomes that of olivine (see same).

**SERUM** — See Blood.

**SESAME OIL (Benne Oil, Gingelly Oil, Gergelim Oil)** — A fatty non-drying oil expressed to the extent of some 50 to 57 per cent. from the seeds of *Sesamum Indicum* or *S. orientale*, N.O. Bignoniaceæ, indigenous in India, where upwards of 5,000,000 acres are under cultivation; also cultivated throughout the East, and to some extent in the countries of South America. It contains about 38.84 per cent. linolein, 48.61 per cent. olein, and 12.55 per cent. saturated compounds (H. P. Kaufmann, *B.C.A.*, B, 1926, 165). The composition has also been given as follows in terms of glycerides: oleic 48.1, linolic 36.8, palmitic 7.7, stearic 4.6, arachidic 0.4, lignoceric trace, and unsaponifiable matter 1.7. Its solidifying point is  $-5^\circ$  C.; sp. gr. 0.921 to 0.925; m.p.  $26^\circ$  to  $32^\circ$  C.; i.v. 103 to 114; sap. v. 188 to 193; and ref. ind. 1.4731 at  $20^\circ$  C. According to W. Adriani, sesame oil also contains up to about 1 per cent. of sesamin ( $C_{20}H_{18}O_6$ ) and smaller proportions of sesamol ( $C_7H_6O_3$ ) of phenolic odour; and samin ( $C_{13}H_{14}O_6$ ). (See *Analyst*, 54, 109 (1929).) It is soluble in ether and carbon disulphide, and used for burning in lamps, also for cosmetics, margarine manufacture, soap-making, perfumery, and as an article of food. Pre-treatment effected by the use of small quantities of filter-aids, followed by the normal refining process, is said to qualify the oil for any purposes to which edible cottonseed oil can be applied. The seeds yield about 50 per cent. of oil.

**SESQUI-** — Prefix denoting one and one-half times, indicative of proportion 2 to 3, for example,  $Fe_2O_3$ .

**SESQUITERPENES** — See Terpenes.

**SEWAGE** — The treatment or disposal of sewage necessarily varies with the quantity and quality to be dealt with, the quality being often affected by trade waste materials. Small quantities can be readily disposed of without other treatment by irrigation, that is, distribution over land where sufficient is available. In this case, the natural

processes of hydrolysis, nitrification, and oxidation rapidly convert the organic constituents into harmless and vegeto-nutritive products.

In larger areas, water is employed as a collecting carrier, and in these cases, after sedimentation in tanks with or without chemical treatment, the effluent can, as a rule, be distributed over land, or carried into running rivers, where that disposal is available and unobjectionable. Chemical treatment depends upon the character of the sewage and the trade refuse that may form part of it. Sometimes milk of lime is used ; in others, ferrous sulphate or sodium manganate ; and in yet others, powdered coke or breeze or dried peat can be used, the precipitated sediment being disposed of by digging into land, or pressed and used as manurial dressing, or alternatively carried away to sea as sludge containing some 85 per cent. water.

The " Simplex " surface aeration process is carried out by use of a specially designed plant by which agitation and exposure to the air, brought about by a circulating operation, purifies the sewage by the atmospheric oxygen to which it is thus exposed.

For large towns and cities, the purification of sewage is often carried out in two stages, the first of which employs treatment in what is known as the " septic tank," through which the sewage passes slowly, and in which the heavier solid parts fall to the bottom and are attacked by anaerobic organisms, thus being ultimately liquefied or turned into gaseous products. In the second stage, the dissolved impurities are disposed of by nitrification and oxidation, which are effected by passing the liquid over a large specially constructed filter or " contact " bed when sufficient land is not available. The artificial filters are made of broken clinker or coke, in which cultivated nitrifying and other bacteria carry out the required purification.

In the so-called " activated sludge " process the whole purification is completed in a tank charged with a quantity of activated sludge to serve as concentrated carrier of the nitrifying bacteria upon which the purification is mainly dependent, the charge of sewage being subjected to a current of air for several days. It is stated that this sludge of colloidal character containing about 5 per cent. of nitrogen finds a keen demand from farmers. Under favourable conditions, on account of the flocculation of the sewage colloids, which are richer in nitrogen than the gross suspended solids, as much as 30 per cent. of the total sewage nitrogen can be recovered in the sludge.

The so-called " bulking " of purified sewage, due to the *carchæsia* and *vorticella* present therein, can, it is stated, be obviated by treatment with certain dyes of the Meldola blue type, these growths being killed by very dilute solutions of the oxazine class of dyes.

For the treatment of sewage containing notable quantities of grease, sulphuric acid or, in its place, nitre-cake has been employed, the fatty acids being set free by such treatment, and forming an oily layer on the top, particularly upon the application of heat. Sulphur dioxide has also been used for the same purpose, and exercises an antiseptic effect.

It is computed that 1,000,000 gallons of sewage yields about 1,300

pounds dry sludge, and that this contains about 90 pounds of nitrogen and 50 pounds of phosphates, and should therefore have a value well above the cost of drying. The high nitrogen content of activated sewage is attributed in the main to removal of ammonia from the sewage by the formation of amino-acids, due to biological processes connected with the protozoa.

Gas-power plants utilize the gas produced by fermentation of sewage sludge, the gas being composed of 67 per cent. methane, 30 per cent. carbon dioxide, and 3 per cent. nitrogen, and having a calorific value of 625 B.Th.U. per 1,000 cubic feet.

Apart from the question of efficiency in the treatment of sewage, all methods must be also regarded from the point of view of economic output.

*References:* *The Principles and Practice of the Dilution Method of Sewage Disposal*, by W. E. Adeney (Cambridge University Press); *Sewage and Sewage Treatment*, by H. E. Babbitt (John Wiley and Sons, New York); and *Wastes*.

“**SEXTATE**” — A British make of cyclohexanol acetate—a high boiling type of solvent for pyroxylin lacquers and rubber.

“**SEXTOL**” — A British make of cyclohexanol for use in soap-making.

“**SEXTONE**” — A British make of cyclohexanone, designed to improve the cleansing power of soap for domestic and textile applications, and for use as a solvent of pyroxylin lacquers.

**SHALE (Carboniferous)** — A fine-grained rock of silt or clay with a cleavage like that of slate, containing an oil-yielding organic material. It occurs in quantity in Scotland, New South Wales (Australia), Colorado, Canada, Sweden, and elsewhere, and is often of petroleum oil-bearing character. The shale of economic value in Scotland is, however, stated to be nearly exhausted. Deposits are also found in Derbyshire, Dorsetshire, Norfolk, Notts, Somerset (between Watchet and the Parrett), while large deposits of “Tasmanite” exist in the Latrobe district of Tasmania, which yield from 40 to 68 gallons oil per ton, and great deposits in Colorado.

The oil obtained by distillation of shale (schist) varies in character with different deposits, ammonium sulphate being obtained as a by-product. Normally the organic matter breaks down into paraffin hydrocarbons, phenols, carbon, and gas, and when pressure is used a higher yield of low boiling hydrocarbons is obtained than by ordinary retorting (F. J. Popham). The English deposits are of a low grade, and contain only about from 3 or 4 up to 10 per cent. volatile hydrocarbons, but it is stated that a process of concentration is available, which may render distillation of the product a profitable operation. The composition of the various deposits of argillaceous nature varies, the ash of the Norfolk Kimmeridge shale, according to Dr. Forbes Leslie, containing 46.10 per cent. silica, 19.90 per cent. alumina, 19.6 per cent. lime, etc.

Many tests have been made on the shales of Colorado, and yields

of 64 gallons (1·5 barrels) of crude shale oil per ton of shale are reported, and the crude shale oil, upon refining, furnishes 15–17 per cent. of gasoline, 30–32 per cent. of kerosene, 18–26 per cent. of gas oil, 15–18 per cent. of light lubricating oils, and 10–12 per cent. of heavy lubricating oils plus paraffin wax. Study of the commercial possibilities of these shales is a part of the programme of the U.S. Government (Bureau of Mines) in its search for new sources of liquid fuels.

“Kukkersite” (the oil shale of Estonia, covering some 770 square miles and estimated at 1,500,000,000 tons) is said to be the richest known, having a sp. gr. of from 1·2 to 1·4, the volatile percentage ranging from 52·5 to 65. The deposits yield from 70 to 80 gallons oil of sp. gr. 0·92 to 0·93 per ton by ordinary retorting. This shale, conjectured to be formed from a soft cyanophycean alga, ranks next to the best torbanites in oil content, and rarely contains more than 35 per cent. moisture. The dry shale contains 47 per cent. bitumen and is marketed in several qualities, the calorific value of average air-dried shale being 9,900 B.Th.U. per pound.

The “Kothla” oil is chiefly used as fuel, but yields light oil and motor spirit upon fractionation, together with a pitch of good quality. About 40 tons of the crude oil is yielded by 200 tons of shale.

The Scottish deposits furnish from 9 up to 22 gallons of oil per ton.

Some shale oils yield to treatment with sulphuric acid, but others with much difficulty. The use of sodium hypochlorite as referred to by A. E. Dunstan holds promise (see his lecture on “The Transmutation of the Chemist” (Institute of Chemistry, December 19, 1930)).

Many oil shales contain small quantities of potash, but so far they have not been worked for its recovery on a paying basis. The organic constituent of shale is known as “kerogen,” and can be extracted from the shale by certain solvents, such as aniline, alcohol, and petroleum. This extract is not an oil, but contains bituminous, resinous, and cellulosic substances, and yields oils upon distillation. Shale oil has a bad character as a carcinogenic agent.

*References:* R. H. McKee on *Shale Oil* (Reinhold Publishing Corp., New York); *Synthetic Liquid Fuels. Oil from Shale*, R.I. 4652 (1950) (U. S. Bureau of Mines, Pittsburgh, Pennsylvania); Naphtha, Petroleum, Schists, and Torbanites.

**SHANKS SYSTEM** — See Extraction.

**SHARK OIL** — See Fish Oils.

**SHEA BUTTER** — A greenish-white solid vegetable fat from the nuts of *Bassia parkii* or *Butyrospermum parkii* (N.O. Sapotaceæ), containing oleic, palmitic, and stearic acids, and some proportions of a phytosterol and a resin, the content of fat being about 46 per cent. It is obtained by boiling the dried nuts in water and can be deodorized by steam; melts at 45° C., has a sp. gr. of 0·9175, sap. v. 179 to 192, i.v. 56·6, and is used as a lard substitute, chocolate fat, and in candle-making. The fatty acids of the saponifiable portion of shea butter are of m.p. 55·5° C. and i.v. 50·8.

There are immense forests of the tree which yields this fat, stretching

behind the oil-palm belt in West Africa, but its use has been somewhat limited up to the present time by its peculiar rubber-like odour and its variable content of unsaponifiable matter, which ranges up to 10 per cent.

Shea-nut cake is of bitter astringent taste, contains saponin and tannin, and has a moderate value as a feeding-stuff for cattle (*Bulletin of the Imperial Institute*, 29, No. 1 (1931)).

**SHEEP DIPS** — There are a great number of makes, some of the best approved consisting of mixtures made from : (1) Carbolic acid, ordinary gas creosote, or other phenolic or cresolic bodies, with soft soap and water ; for example, 5 pounds of soft soap dissolved in 3 quarts of 97 per cent. carbolic acid and 100 gallons water. (2) Flowers of sulphur with slaked lime and water. (3) Aqueous extract of offal tobacco. (4) Arsenious compounds, alkali, and sulphur worked up with a certain quantity of water. (5) Tobacco extract, sulphur, and water in emulsified form. (6) Tar oil, tobacco extract, soda-ash, and water, with or without soft soap. (7) Suspensions of D.D.T.

**SHELLAC** — “Stick lac” is either a secretion or excretion of the lac insect (*Coccus lacca*, otherwise *Tachardia lacca*) which abounds in the forests of Assam, constituting the resinous covering on the branches of various jungle trees, the variety from *Zizyphus xylopyrus* having the greatest moisture content, which ranges from 1.0 to 6.1 per cent. Siam is stated to rank next after India as the world's largest producer. From it is prepared “seed lac,” that is, lac from which the wood has been removed. Lac dye (now obsolete) is the colouring matter of the insect, and shellac is the resin prepared by melting and straining. The sp. gr. of orange shellac is 1.08 to 1.13, acid value about 60, and it decomposes if heated much above 100° C. It is soluble in ammonia and in solutions of sodium carbonate, borax, and other alkalis, certain organic acids, and ketones, while shellac varnish consists of the resin dissolved in alcohol of high-proof character. It is stated to polymerize under heat, as shown by its decreased solubility in alcohol. The Indian production of shellac amounts to some 20,000 tons per annum.

“Garnet lac” is made from the residue left after the squeezing process ; “Button lac” is shellac fused in shape of buttons, while “white” or “bleached” shellac is prepared from the orange shellac by dissolving it in dilute sodium carbonate and bleaching with sodium hypochlorite or chlorine solution, thereby destroying the red lac dye. Subsequently the lac is reprecipitated from the solution by sulphuric acid, then washed and kneaded in hot water.

The pure resin is stated to contain from 22 to 24 per cent. of a trioxypalmitic acid named aleuritic acid, and a yellow dye (erythrolaccen), which gives a red solution with alkalis.

A Burmese lac named “Thitsi” is prepared from the stems of *Melanorrhæa usitata* Wall. Indo-Chinese lac is stated to be tapped from *Rhus succedanea* L. fil., and to contain a substance named laccol, which is readily reduced to hydrolaccol ( $C_{23}H_{40}O_2$ ) of m.p. 63° to 64° C. ; this substance in turn being isomeric with hydrothitsiol and a

higher homologue of hydrourushiol, which, together with urushiol ( $C_{21}H_{32}O_2$ ), form the main constituents of Japanese lac.

Formosa lac comes from *Semeocarpus vernicifera*, and another product from *Rhus ambigua* Lav., or *Rhus orientalis* Sohn, both containing laccol; whereas Chinese lac (probably from *Rhus vernicifera*) contains mainly urushiol ( $C_{21}H_{32}O_2$ ), which is reported to have a toxic action higher than that of laccol and thitsiol.

In coloured alcoholic solution shellac has been advocated as a good ink for marking laboratory glass vessels.

Shellac is the chief constituent of the Indian-made mica-board (micanite) and is used in the process engraving and lithographing trades, as a stiffening material in the hat trade, in leather-dressing, in electrical apparatus and gramophone record-making, varnishes, and the manufacture of sealing wax, etc. (See "Albertol," Lacquer, and Sealing Wax.)

**SHERARDIZING** — See Metals.

**"SHIRLAN"** — See Salicylanilide.

**SHODDY** — Wool waste and clippings of wool fabrics, utilized by grinding with toothed rollers, and making up with or without new wool into rugs, inferior cloths, flannels, etc. Cotton content of the waste and fabrics is destroyed by treatment with dilute sulphuric acid.

**"SICALITE"** — A kind of French-made plastic material.

**SICCATIVES** — Agents which promote drying, more particularly the so-called "driers" used in connection with varnishes, oils, and paints, such as manganese borate, resinate, and oleate; cobalt resinate and cobalt linoleate, etc. (See Linseed Oil, Oils, and Varnishes.)

**SIDERIN YELLOW** — Basic ferric chromate, a pigment used in metallurgy and as a glaze and colouring matter for glass and porcelain.

**SIDERITE (Spathic Iron Ore)** — A mineral carbonate of iron ( $FeCO_3$ ), found in Canada and some parts of the United States (crystal system No. 3, and sp. gr. 3.8).

**SIENNA** — A yellowish clay coloured by metallic oxides (iron and manganese), used as a pigment. (See Ochre.)

**SIEVE** — See Separation.

**SIFTING** — See Separation.

**SILAGE** — See Ensilage.

**SILANES** — Silicon Hydrides. (See Silicon (Silanes).)

**SILICA** — See Clays, Porcelain, Refractories, Silicon, and Zeolites.

**SILICA GELS** — Colloidal Silica. (See same under Silicon.)

**SILICANES** — See Silicon (Silicanes).

**SILICATE OF SODA** — See Sodium (Silicate).

**SILICATES** — See individual silicates.

**SILICIC ACID** — See Silicon (Silicic Acid).

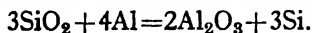
**SILICIDES** — See Silicon (Silicides).

**SILICON (Si) and its Compounds** — Atomic weight, 28·06. See Elements for other data ; accompanying Charts ; and also Calcium, Lime. Silicon is not a metal, but it is known both in the forms of a brown powder and in a crystalline condition, which latter form greatly resembles a metal. Its compounds are abundant and widely distributed in nature. Combined with oxygen as silica ( $\text{SiO}_2$ ), it is found in the forms of *agate*, *amethyst*, *chalcedony*, *cristobalite* (in volcanic rocks), *flint*, *jasper*, *onyx*, *opal*, *quartz*, *rock crystal*, *sand*, and *tridymite*, while in other combinations it helps to make up the composition of clay soil, and many rocks, including beryl, serpentine (a magnesium silicate  $\text{Mg}_3\text{Si}_2\text{O}_7$ ), peridot (another magnesium silicate  $\text{Mg}_2\text{SiO}_4$ ), and felspars of varying composition. (See Clay, and Zeolites.) Among other forms is found in combination with water ( $\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ ), in the form of *kieselguhr*.

The three crystalline (polymorphic) forms of silica are known as quartz of sp. gr. 2·65 ; cristobalite, sp. gr. 2·32 ; and tridymite, sp. gr. 2·30. The atomic structures of a number of silicate minerals have been worked out by the X-ray method of W. L. Bragg and others. (See *Annual Reports of the Progress of Chemistry*, 26, 253 (1929).)

To obtain silicon in the free state, several processes are available, in one of which a mixture of potassium fluosilicate and metallic potassium is strongly heated, when the potassium replaces the silicon, which is thus set free and obtained by dissolving out the potassium fluoride with water :  $\text{K}_2\text{SiF}_6 + 2\text{K} = \text{Si} + 6\text{KF}$ . As thus prepared it is a dark brown amorphous powder with a sp. gr. of from 2·0 to 2·15.

It is obtained in needle-shaped crystalline form by the "Goldschmidt Thermit" reaction (see "Thermit" Process) of a mixture of finely divided quartz and aluminium metal upon ignition :



The temperature rises sufficiently to melt the aluminium oxide, which upon cooling is a glass. There is a variation of the mixture in which sulphur is incorporated.

Silicon is insoluble in water, hydrochloric and nitric acids, but is soluble in hydrofluoric acid and alkalis. With alkalis, hydrogen gas is evolved, a method which has been used industrially to produce hydrogen.

Silicon is used in alloys, such as ferro-silicon, for admixture with molten steel, and for the reduction of various oxides to their metals (see Perkin Medal Address by F. M. Becket (*Ind. Eng. Chem.*, 16, 197 (1924))).

Quartz crystals find uses not only as gems, but also for certain optical purposes ; while sodium silicate ( $\text{Na}_2\text{SiO}_3$ ) as a manufactured article finds many industrial applications. (See Sodium (Silicate).)

**Silanes** — Four compounds of silicon with hydrogen are known, silane ( $\text{SiH}_4$ ), a colourless gas, which is decomposed by alkaline hydroxides,

## SILICON-CONTAINING SUBSTANCES

## CHARTS SHOWING PRINCIPAL APPLICATIONS

Arranged by the Editor.

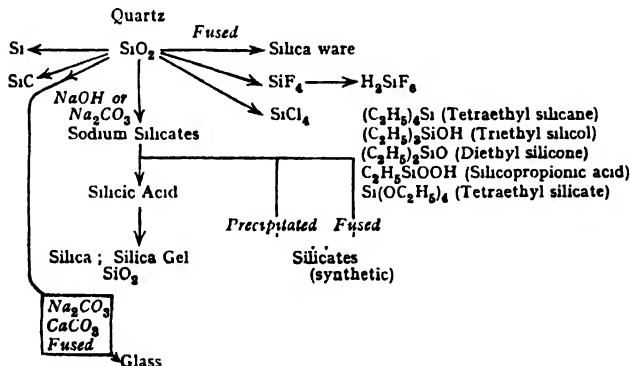
## CHART I.—OF NATURAL OCCURRENCE

Principal Uses	As Silicon Oxide (principally)	As Aluminosilicates
Abrasives	Quartz	Feldspars, principally potassium aluminosilicate
Refractories	Rock quartz	Micas, principally potassium aluminosilicate
Structural materials	Vein quartz	Leucite, principally potassium aluminosilicate
Stone, brick, tile	Amethyst	Garnet
Stoneware and porcelain	Agate	Pyroxene } generally with one or more metallic elements
Portland cement	Chalcedony	Hornblende }
Metallurgical slags	Jasper	Tourmaline }
Glass	Opal	Zeolites
	Onyx	Sillimanite, principally aluminum silicate
Fused silica ware	Flint	Andalusite, principally aluminium silicate
Silica gel	Quartzite	Beryl, principally beryllium aluminosilicate
	Sandstone	
Alloys	Quartz sand	
Soluble silicates	Petrified wood	
Hydrofluosilicic acid	Infusorial earth, diatomaceous earth, tripolite	
		Igneous and their Metamorphosed Rocks
	As Hydrated Magnesium Silicate (principally)	Granite
	Serpentine	Basalt
	Talc	Obsidianite
	Asbestos	Lava
	Meerschaum	
		Sedimentary and their Metamorphosed Rocks
	As Aluminum Fluosilicate	Shale
	Topaz	Slate
		Soils
	As Zirconium Silicate	Clay, Kaolinite, Fuller's Earth
	Zircon	
	As Calcium Silicate	
	Wollastonite	

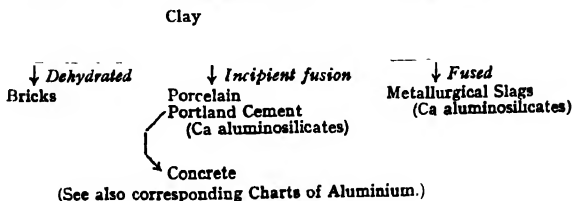
SILICON ELEMENT  
28 per cent. of the earth's crust

Or, when expressed as  $\text{SiO}_2$ , about  
60 per cent. of the earth's crust

## CHART II A.—OF MANUFACTURE FROM QUARTZ



## CHART II B.—OF MANUFACTURE FROM CLAY



giving the corresponding silicates and evolving hydrogen:  $\text{SiH}_4 + 2\text{NaOH} + \text{H}_2\text{O} = \text{Na}_2\text{SiO}_3 + 4\text{H}_2$ ; disilane ( $\text{Si}_2\text{H}_6$ ), a colourless gas; trisilane ( $\text{Si}_3\text{H}_8$ ), a colourless liquid, of b.p.  $53^\circ\text{C}$ .; and tetrasilane ( $\text{Si}_4\text{H}_{10}$ ), a colourless liquid of b.p.  $109^\circ\text{C}$ .

**Methylchlorosilane** ( $(\text{CH}_3)\text{SiCl}$ ) vapour reacts almost instantly with the cellulose (through hydroxyl groups of the latter) of cotton fibres, covering the fibre with a layer of  $(\text{CH}_3)_3\text{SiOR}$ , which repels water as an oil does. Other fibres, including paper—as well as porcelain and glass—may be similarly treated.

**Silicon Dioxide or Silica** ( $\text{SiO}_2$ ) may be prepared in the laboratory in crystalline form or as a white powder by a variety of methods, as when, for example, amorphous silicon is burned in the air. It is fusible in the oxyhydrogen flame, when it melts to a transparent glass-like mass; is insoluble in water, and the only acid that will dissolve it is hydrofluoric acid; it is, however, soluble in alkalis.

Artificial crystals of quartz weighing up to 0.25 pound have been produced in 30 days or less by A. C. Walker and E. Buehler (*Ind. Eng. Chem.*, **42**, 1369 (1950); *Sci. Monthly*, **69**, 149 (1949)) of the Bell Telephone Laboratories using an autoclave, an alkaline solution, nutrient quartz, a seed crystal of quartz at a temperature of approximately  $400^\circ\text{C}$ .

It is generally stated that when fused silica is heated above  $1,000^\circ\text{C}$ . up to  $1,500^\circ\text{C}$ ., it is transformed gradually into cristobalite, a change which is completed in several hours after continuing the heat to  $1,500^\circ\text{C}$ ., and the final product is stated to be probably tridymite: further, that quartz begins to soften at about  $1,650^\circ\text{C}$ ., and becomes a viscous fluid at from  $1,710^\circ$  to  $1,750^\circ\text{C}$ . Silica is strongly volatile at a temperature slightly above its melting-point.

Above  $870^\circ\text{C}$ . silica enters a metastable condition gradually changing into tridymite, the change reaching completion in some hours above  $1,400^\circ\text{C}$ . but below  $1,470^\circ\text{C}$ ., but only in the presence of a flux such as sodium tungstate, and at  $1,470^\circ\text{C}$ . tridymite is stable. If, however, quartz be heated to  $1,250^\circ\text{C}$ . in the absence of a flux, cristobalite formation commences and proceeds with greater velocity at higher temperatures, and at temperatures above  $1,470^\circ\text{C}$ . cristobalite is said to be stable, but between that temperature and  $1,250^\circ\text{C}$ . it is metastable and slowly changes into tridymite. Tridymite melts at  $1,670^\circ\text{C}$ . and cristobalite at  $1,710^\circ\text{C}$ .

Acid-proof (although attackable by alkalis and metallic oxides), abraded with difficulty, and with great resistance to temperature shocks, silica-ware is an important substitute for glass in many cases. Silica glass is insoluble in boiling water, but is permeable to gases at high temperatures. It is an ideal electrical insulating material. (See Ganister, Refractories, and "Vitreosil.")

The density of transparent fused silica is 2.22, and that of the opaque variety 2.07. Its coefficient of thermal expansion is less than that of the best glass of the "Pyrex" type, and its crushing strength has been reported as between that of granite and blue brick, namely, 7 tons per square inch.

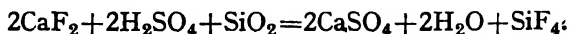
Silica of varying qualities is largely used in admixture with paints and rubber articles, also in making soaps, polishes, pottery, phosphorus, non-inflammable materials and packings, as a flux in metallurgy, making silica bricks (quartzites being chiefly used for this particular purpose), and in the manufacture of glass and carborundum.

**Colloidal Silica** results from the decomposition of sodium silicate solutions by acid, and can also be prepared by passing an electric current through a solution of sodium silicate, using diaphragms which permit of the expelled soda being driven out through them in such a way that backward diffusion does not occur. It is thus possible to obtain solutions up to 30 per cent. strength, and these by polymerization give a "gel," which, upon drying, constitutes an inert highly electro-negative substance found to have extraordinary powers as an adsorbent. The silicic solution produced by the electro-osmose process is stated at the moment of its preparation to have a molecular weight corresponding to the formula  $H_2SiO_3$ . **Silica "gels,"** prepared by several methods, are the subjects of a number of patents. They are used industrially for the elimination of hydrogen sulphide from gas, the refining of mineral oils (removing the sulphur content), and in the United States in connection with air conditioning and the iceless refrigeration of railway freight cars. They are also used for the recovery and refining of benzol from coke-oven gases (the gas entering the gel plant under the same conditions as it would enter the oil washers), thus removing the whole of the light oils and any water. Another application is for the dehydration of air for blast furnaces. Some natural siliceous earths of colloidal character are used in some of these applications, such as oil refining. (See *Silica and the Silicates*, by J. A. Audley (Baillière, Tindall and Cox, London); *Soluble Silicates in Industry*, by J. G. Vail (Reinhold Publishing Corp., New York); and Adsorption.)

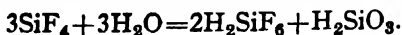
**Silicic Acid**  $(Si(OH)_4)$  is the best-known member of several weak polybasic acids and hydrates which are formed by combination of silicon dioxide and water, and can be obtained either in solution or in gelatinous form, in both of which it behaves as a colloid. The formula  $Si(OH)_4$  is attributed to the tetrabasic orthosilicic acid. Preparations of silicic acid, as obtained from various silicates, lose water under diminished pressure and yield definite silica hydrates.

**Silicates** are discussed under the individual metal. See Sodium (Silicate).

**Silicon Fluoride**  $(SiF_4)$  is a colourless, fuming gas prepared by heating a mixture of sulphuric acid, powdered fluorspar, and white sand :



The same compound is formed direct by bringing silicon into contact with fluorine when it takes fire. The gas can be liquefied to a clear colourless state, and when brought into contact with water, decomposition takes place, dibasic silicic acid being precipitated as a gelatinous mass accompanied with hydrofluosilicic acid in solution :



**Hydrofluosilicic Acid** ( $\text{H}_2\text{SiF}_6$ ) may also be obtained as a colourless fuming liquid by passing gaseous silicon tetrafluoride into water, and separating the solution of hydrofluosilicic acid from the precipitated silicic acid. It is usually put up in the form of a solution of sp. gr. 1.350, although it can be concentrated to a greater extent. It is very corrosive and (in common with fluosilicates) is employed in the ceramic industries, in making concrete floors, certain technical paints, and in solution of some 25 to 30 per cent. strength as an antiseptic and fungicide. Some of the fluosilicates or salts of hydrofluosilicic acid are used to render stonework resistant to atmospheric decay, while others, in common with the free acid itself, are used as insecticides and vermicides.

**Silicon Tetrachloride** ( $\text{SiCl}_4$ ) is produced when silicon is heated in a current of chlorine at  $500^\circ\text{C}$ . and upwards. The silicon burns and the gaseous tetrachloride is formed direct; or it can be made by passing chlorine gas over a mixture of silica and carbon in an electric furnace (at  $1,000^\circ\text{C}$ .), when the following change takes place:  $\text{SiO}_2 + 2\text{C} + 2\text{Cl}_2 = 2\text{CO} + \text{SiCl}_4$ . The gas can be condensed by cooling, as a colourless liquid which fumes in the air, and is decomposed by water into silicic and hydrochloric acids. Its sp. gr. is 1.50, b.p.  $57.6^\circ\text{C}$ ., and it has been used for producing smoke screens.

**Silicon Hexachloride (Silicon Trichloride)** ( $\text{Si}_2\text{Cl}_6$ ) is formed by passing the vapour of silicon tetrachloride over strongly heated silicon:  $3\text{SiCl}_4 + \text{Si} = 2\text{Si}_2\text{Cl}_6$ . It is a colourless, mobile fluid of b.p.  $144^\circ$ , crystallizes at  $-1^\circ\text{C}$ ., and, when boiled, its vapour spontaneously ignites in contact with air.

**Silicides** — Silicon unites with aluminium, iron, zinc, copper, calcium, magnesium, and some other metals, forming compounds named *silicides*. It also unites with carbon to form the hard crystalline substance silicon carbide ( $\text{SiC}$ ), known otherwise as "Carborundum" (see Abrasives), and enters fundamentally into the composition of various kinds of glass which are, in reality, insoluble compound silicates. For the most part the reactions involved in making silicides require such high temperatures that the electric furnace alone is used as a means of attaining the same.

**Silicanes** — Silicon acts as a substitute for carbon in many organic compounds, and among these are tetramethyl silicane or silicon tetramethyl ( $\text{Si}(\text{CH}_3)_4$ ), a mobile liquid of light nature, and tetraethyl silicane or silicon tetraethyl ( $\text{Si}(\text{C}_2\text{H}_5)_4$ ), both of which burn with a bright light and emit white clouds of silica.

**Silicon Esters** — The name given to the alkyl and aryl silicates and various mixtures: methyl (ortho) silicate (tetramethoxy silicon) ( $\text{Si}(\text{OCH}_3)_4$ ), of b.p.  $122^\circ\text{C}$ .; ethyl (ortho) silicate (tetraethoxy silicon) ( $\text{Si}(\text{OC}_2\text{H}_5)_4$ ), of b.p.  $165^\circ\text{C}$ .; and higher members are used industrially. Silicon ester paint media and stone preservatives are prepared by the controlled hydrolysis of ethyl silicates. (See *Chemical Industries*, 39, 145 (1936); Paints, and Stone Preservation.)

**Silicon Bronze** — An alloy of silicon, copper, and tin used for telegraph and telephone wires.

**Silicones** — See same.

(See Clays, "Carborundum," Ferro-Alloys, Glass, and Sodium (Silicate).)

**SILICONES** are substances based on oxygen-silicon linkages with organic groups attached to the silicon atoms. The variations that are possible from this fundamental arrangement result in substances of decided novelty and variety, namely, (1) oils and greases, (2) artificial rubber *i.e.*, elastomers, (3) resins and baking enamels, and (4) water repellents. The high electrical insulating property of these materials attracted early attention, and along with this property they show remarkable resistance to heat, to moisture, and to many chemicals. Such properties permit a marked reduction in weight and size of electrical machines. Some silicones have unusually good bonding power on steel, glass, mica, and asbestos, since they are sticky, thermoplastic, and when cured yield a tough, hard product. Enamelled surfaces for protective and decorative effects are thus possible. The oil types have viscosities that change remarkably little with temperature, which is a desirable characteristic of lubricants subjected to very low or very high temperatures.

In characteristics the silicones lie between the synthetic organic resins on the one hand, and porcelain, glassy, vitreous enamels on the other; for example, exposure to a temperature of 260° C. (500° F.) for a long time results in only a slight loss of adhesion and flexibility and no change in gloss. A further advantage is that these properties are retained at low temperatures, even down to -50° C. (-60° F.)

Silicones are made by the reaction of silicon tetrachloride ( $\text{SiCl}_4$ , b.p. 58° C.) and Grignard reagent ( $\text{RMgCl}$ , where R is a hydrocarbon radical such as  $-\text{CH}_3$  or  $-\text{C}_6\text{H}_5$ ), followed by hydrolysis to form  $\text{RSi}(\text{OH})_3$ ,  $\text{R}_2\text{Si}(\text{OH})_2$ ,  $\text{R}_3\text{Si}(\text{OH})$ . The first two types are used as resins and baking enamels, and the last two as greases and oils. The commercial launching of silicones occurred about 1943, partially as a result of the demand in World War II for materials possessing the unusual properties described. They had been studied by Kipping for for some forty years previously in laboratory experiments.

*References:* E. G. Rochow, *Introduction to the Chemistry of Silicones* (John Wiley and Sons, New York); *Silicones and Other Organic Silicon Compounds*, by H. W. Post (Rheinhold Publishing Corp., New York).

**SILICOSIS** — The name of an occupational disease of tubercular character brought about by the inhalation of dust in refractory industries, and metal grinding. The mortality rate in respect of this trouble has been decreased by the substitution of the "carborundum" wheel for the grit-stone wheel. Rules relative to this matter can be obtained from H.M. Stationery Office. The first World Conference on the Incidence, Causation and Prevention of Silicosis was held in Johannesburg in 1930.

**SILK** — The fibrous material containing a nitrogenous substance named *sericin* or *fibroin* ( $\text{C}_3\text{H}_7\text{O}_3\text{N}$ ), in which the silkworm (*Bombyx mori*) envelops itself before passing into the chrysalis state. This is coated

with a kind of wax which has to be removed in the process of silk-dyeing. Persoz' reagent (see same) dissolves silk. Stannic chloride is used for weighting silk, the de-gummed fibres being steeped in a solution of that compound and subsequently washed.

In 1912, the world's production of raw silk was approximately 56 million pounds; in 1922, 68; in 1932, 84; and in 1938, 62; and the per cent. produced by Japan was respectively 43, 61, 85, and 87.

*References:* *Silk and the Silk Industry*, by J. Schober (Constable and Co., London).

**SILK SUBSTITUTES** ("Artificial Silk," "Rayon") — When cotton cloths or yarns, in a stretched condition (so as to prevent shrinking of the fibres), are exposed to the action of a solution of caustic soda of from 18 to 25 per cent. strength a silk-like lustre is imparted to them. The cotton fibres are naturally flattened hollow ribbons or tubes, and under this treatment they swell up, by thickening, into cylinders without practically any hollow spaces, stronger than the unprepared materials, and more easily susceptible of dyeing. This treatment is known as **mercerization**, which increases the ripping strain, the weft being less affected than the warp of fabrics made from the prepared material. Any excess of soda is washed out from the mercerized product before use, and in some cases halogenated fatty acids are employed in connection with the mercerization process so as to increase the silky lustre of the products. Mercerized cotton is practically a simple form of silk substitute, and one form of artificial silk can be prepared by using this mercerization reaction as the starting point and treating the product with the proper solvent (see below).

Silk substitutes are made by several distinct methods, the oldest of which is the so-called **nitrocellulose process** (Chardonnet's), in which thick solutions of that substance in a mixture of alcohol and ether were forced by hydraulic presses through capillary glass tubes of very small bore, and the resulting threads twisted on bobbins. As now practised, these bobbins of nitrocellulose, made from cotton or wood-pulp, are transformed into hanks, which are then subjected to chemical treatment by ammonium, sodium, or calcium sulphide in order to denitrate them, whereby the nitrocellulose is changed into cellulose, thereby suffering a loss in weight of some 35 per cent.

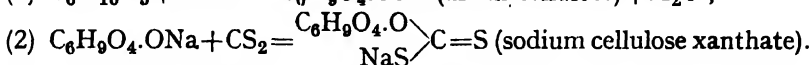
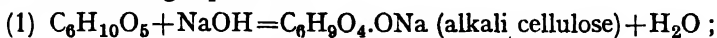
"Thiele Silk," which is a French product of long standing, is made by the so-called **cupra-ammonium process**, conducted by dissolving cellulose (cotton linters or bleached wood-pulp) in ammoniacal cupric oxide solution and forcing the solution through small holes into dilute acid, by which means the copper is removed and regenerated cellulose is precipitated or coagulated as it leaves the spinneret, and after some purification by a "stretch" spinning process yields the finer counts of "artificial silk." This process, however, is little used, only some 4 per cent. of the world's production being obtained thereby.

The so-called **viscose process** (using cotton or wood-pulp as raw material) possesses a predominating position in commerce. There are other materials from which cellulose can be prepared and utilized by this process, including the residual begasse (from sugar manufacture),

Tasmanian stringy-bark pulp (*Eucalyptus obliqua*), and New Zealand hemp fibre, which contains 70·25 per cent. cellulose calculated on the moisture-free material.

Cross and Bevan found that when mercerized cellulose, prepared from spruce or other wood-pulp and bleached cotton linters by treatment with 18 per cent. strength caustic soda solution, is acted upon by carbon disulphide a swollen yellowish mass consisting of sodium cellulose xanthate is produced. This substance is subsequently dissolved in water or weak caustic soda and treated with sulphuric or other acid, thus effecting the reprecipitation of the cellulose as a gelatinous mass to which the name of "viscose" has been given.

These chemical changes concerning alkali-cellulose can be expressed by the following equations :



The viscose produced as described, after ripening and some purification, is used in the manufacture of "artificial silk" by drawing the coagulated viscose on to bobbins, then washing, drying, sizing, and weaving as required. One ton of sulphite pulp yields about 1,500 pounds of product. The spinning jets used in manufacturing silk substitutes are made of platinum-iridium or of gold with 10 per cent. platinum. (See *Viscose Rayon Production*, by D. L. Pellatt (Emmott and Co., Manchester).)

The variety known as "acetyl" or "acetate" silk is made by treating cellulose with acetic acid and acetic anhydride or acetyl chloride in presence of a catalyst such as sulphuric acid or zinc chloride, and the acetylcellulose thus produced containing about 50 per cent. acetyl is spun from an acetone solution in the ordinary manner. This variety consists of cellulose acetate and is stated to approach more nearly to natural silk than any other, and the process is of growing importance.

The swelling and acetylation of cellulose has been studied by Bernoulli and others, who conclude that the acetylation proceeds in stages, thus, cellulose monoacetate ( $\text{C}_6\text{H}_5(\text{OH})_4\text{OOCCH}_3$ ), and triacetate ( $\text{C}_6\text{H}_5(\text{OH})_2(\text{OOCCH}_3)_3$ ). They also observe that in the case of viscose the affinity for substantive dyes decreases as acetylation proceeds.

The different kinds of "artificial silk" may be distinguished by treatment with pure concentrated sulphuric acid and iodine ; nitro-cellulose dissolves with a purple colour, cupra-ammonium silk with a light blue colour, acetate silk with a yellow colour, and viscose silk with a dark blue colour.

By increasing the size of the apertures through which the viscose or cellulose solution is forced, a kind of artificial hair can be produced available for making hats and use in upholstery. Again, by changing the shape of the apertures a straw-like form can be made, and by widening the slit, strips of material are produced, which can be used as a kind of artificial leather or cloth, and as ribbons or sheets. Methods have also been devised in which net and forms of artificial lace can be

produced in one operation, or again as a thin wrapping material named "Cellophane."

Viscose dries to a hard, horn-like mass, and is further employed as a substitute for making articles resembling celluloid and ivory, and when mixed with zinc oxide or clay it makes a harder substance called "Viscoid."

**Nylon** (see same) is one of the most popular substitutes for silk. (See also "Orlon.")

The **waterproofing** of silk substitutes is effected by several methods, one of which is based upon treatment of the yarn with formaldehyde and lactic acid, and another on treatment with mineral compounds during the desulphurization of the skeins.

**Dyeing** — Silk substitutes are stated to have a greater affinity for dyestuffs than cotton, but those colours which are most fast on the usual fibres are the most fugitive on the cellulose acetate fibre. At one time cellulose acetate was dyed with direct, vat, and sulphur colours by the addition of caustic soda to the printing pastes, and it was known to possess the property of absorbing some simple primary amine bases, such as aniline, para-nitraniline, etc., which by various treatments, such as oxidation or diazotizing, gave colouring matter to the fibres. These products, however, were not very satisfactory, but as research work progressed, the use of soluble compounds produced by Green and Saunders from the strongly basic dyestuffs by use of the omega-sulphonic acid group (in which the solubilizing acid group is not attached directly to a benzene or fused-benzene nucleus, but to an aliphatic side chain) overcame some of the difficulties previously encountered. This group is split off gradually by hydrolysis in the dyeing operation, thus yielding the actual colouring matter to the fibre, which then readily absorbs it.

For the realization of a fuller range of differently coloured compounds which will hydrolyse with reasonable limits under ordinary working conditions so as to attain compatibility of dyeing properties while maintaining the requisite fastness of colour, resort was made by G. H. Ellis to other supplementary methods of procedure, now known as the "S.R.A." methods. These rely upon "physical solubilization" or "colloidal dispersion" of ordinarily insoluble colouring matters in such wise as to render them properly available to the fibre to be dyed. The designation "S.R.A." is derived from sulpho-ricinoleic acid—one of the solubilizing agents employed—and the colours are prepared in the form of 10 per cent. pastes which incorporate the colouring matter together with the dispersing agent ready for use.

It is also possible, using suitable cotton dyestuffs, to obtain by single bath-dyeing on mixed goods of "Celanese" and cotton or cellulosic artificial silk either totally contrasting shades, blending shades, or uniform effects as may be desired. Among dyes which can be used satisfactorily in the dyeing of cellulose acetate are "Duranol" and "Dispersol."

Silk substitutes are used extensively in combination with cotton materials.

In 1932, the world's production of rayon yarn was 515,000 pounds ;

in 1938, 990,000. Of the latter amount the U.S.A. produced 26 per cent., Japan 21, Germany 14, Great Britain 11, and Italy 10.

*References:* *The Rayon Industry*, by M. H. Avram (Constable and Co., London); *The Manufacture of Artificial Silk*, by E. Wheeler (Chapman and Hall, London); *Artificial Silk*, by E. Reinthaler, translated by F. M. Rowe (Chapman and Hall, London); *Acetate Silk and its Dyes*, by Chas. E. Mullin (Constable and Co., London); *Artificial Silk (Rayon): Its Manufacture and Uses*, by T. Woodhouse (Sir Isaac Pitman and Sons, London); Cellulose, "Cordura," Nylon, "Orlon," and Rayon.

"**SILLAX**" — A British make of laboratory porcelain.

**SILLIMANITE** — A mineral (of which deposits are found in India, at Nongmaweit), being anhydrous aluminium silicate, occurring in crystalline form in gneisses and crystalline schists, while other minerals named *fibrolite*, *andalusite*, and *cyanite* of distinct physical characters can be converted into *sillimanite* by heating to above  $1,320^{\circ}\text{C}$ . It has valuable properties as a refractory, and it is reported that a stable silicate of crystalline form of the formula  $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$  can be prepared by heating china clay (kaolin) to from  $1,200^{\circ}$  to  $1,300^{\circ}\text{C}$ . with or without a reducing agent. Brown and Greig have represented that this crystalline body has the composition  $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ , and they name it "mullite," after the crystals found in some natural rocks at Mull. There has been much divergence of views as to the constitutional changes which occur in clays upon heating. According to J. W. Greig, cyanite, andalusite, and sillimanite are all decomposed into mullite and silica, or into mullite and a silicious liquid (probably cristobalite), when sufficiently heated.

Mullite and sillimanite are said to be almost identical crystallographically and optically. Mullite appears to be invariably formed by the interaction of silica and alumina at high temperatures, and can be produced from bauxite, diaspore, gibbsite, and kaolin, or mixtures of them. It exhibits a strong tendency to crystallize, but by careful preparation of "melts" can be prepared of strong character of the approximate composition  $3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ , strongly resistant to acids and slag action, thus admitting of employment for making bricks less liable to "spalling" than either silica or magnesite brick.

Kaolin is stated to break down at  $600^{\circ}\text{C}$ ., a silicate, presumably  $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ , stable up to  $900^{\circ}\text{C}$ ., being formed, and above this temperature mullite results, which in turn undergoes decomposition above its melting-point ( $1,810^{\circ}\text{C}$ .), corundum being formed. (See Kaolin.)

Sillimanite is strong and tough, exhibiting low electrical conductivity, freedom from volume change, of neutral reaction, and resistive to corrosive slags, etc. Experimental work has demonstrated that sillimanite is superior to fire-clay for glass-making pots and furnace bricks exposed to great heat, and very useful for repairing the bad places in old furnaces, the best results being obtained with sillimanite bonded with from 10 to 25 per cent. ball-clay. The same mixtures are also used for making semi-permanent moulds for repetition castings in iron, steel, and other metals. (See Silicon (Oxide), and Refractories.)

"**SILMANAL**" — A permanent-magnet alloy of silver, manganese, and aluminium with unusual properties for special applications. It is ductile, malleable, and machinable and can withstand severe demagnetization because of its high coercive force and low residual flux. A magnetizing force of 20,000 oersteds or 40,400 ampere-turns per inch of length is required for this alloy, making long pieces difficult to magnetize. "Silmanal" is used where magnets are subjected to extreme demagnetizing effects, such as heavy A.C. fields. (See W. E. Ruder (*Iron Age*, 157, 65 (May 9, 1946).))

"**SILOCEL**" — A high temperature insulating material.

"**SILOXEN**" ( $H_6O_3Si_6$ ) — An enormously porous substance possessing powerful absorbing quality, prepared from calcium silicide ( $CaSi_2$ ).

"**SILOXICAN**" — An amorphous refractory powder, described as a silicon oxycarbide formed in certain amount in the manufacture of carborundum at temperatures above  $1,500^\circ C$ . It is of general formula  $(SiC)_nO$ , when  $n$  varies from 1 to 7, and can be used for making furnace linings.

"**SILUMIN**" — An alloy of sp. gr. from 2.5 to 2.65, great hardness and tensile strength (about 12.7 tons per square inch), consisting of about 88 per cent. aluminium and 12 per cent. silicon. It is less attacked by wet steam and strong nitric acid than pure aluminium, is very useful for making steam kettles and similar apparatus, and of great value in the motor industry.

**SILVER** (Ag) and its Compounds — Atomic weight, 107.880. See Elements for other data. Silver occurs in nature in the metallic state and in combination in a great number of minerals, including *argentite* or *silver glance*, as silver sulphide ( $Ag_2S$ ); in *horn silver*, as chloride ( $AgCl$ ); as silver sulphide associated with other metallic sulphides in *pyrargyrite* ( $Ag_3SbS_3$ ), *stephanite* ( $Ag_4SbS_4$ ), *proustite* ( $Ag_3AsS_3$ ); as bromide ( $AgBr$ ) in *bromite* or *bromyrite*; whilst *iodite* (*iodyrite*) is a Spanish silver iodide of mineral nature containing over 46 per cent. silver. It is present also in many lead ores, notably galena. The world's supply comes from the U.S.A., Canada, Mexico, South America, and Japan. (See also Embolite.)

To obtain metallic silver from argentiferous galena, which is the chief source, resort is had to the process described as *cupellation*, following upon smelting of the silver ores with lead or materials yielding lead. This process depends upon the fact that the silver can be concentrated into a small portion of lead by crystallization, and then the mixture is exposed to a strong blast of air, thus oxidizing the lead into litharge, which fuses, and is then drawn off or absorbed by the porous bed of the furnace, leaving the silver behind. The furnace bed is made of bone ash so as to be absorbent, and is known as *cupel*. (See Cupellation.)

In the Mexican amalgamation process, crushed silver ore is ground in water to a state of fine division and, after the incorporation of from 3 to 5 per cent. common salt, spread in a widely distributed manner

over a circular space of floor. A day or so later, some metallic mercury is added, together with a proportion of magistral (see same), the whole being well worked up together, and fresh mercury added from time to time. The silver is thus gradually converted into silver chloride, and this, being soluble in sodium chloride, is reduced by the mercury to the metallic state and forms an amalgam therewith. The amalgam is subsequently collected, washed, and subjected to distillation, the mercury passing over and being recovered, while the silver is left behind.

There are a number of other methods which are adapted to the several requirements according to the composition of the ore from which the silver has to be obtained. One of these alternative processes consists of roasting the ore with salt, extracting the silver chloride thus formed with sodium thiosulphate, and precipitating the silver content of the solution as sulphide, from which the metal is obtained by roasting in a reverberatory furnace.

Another depends upon extraction with alkali cyanides and precipitation of the metal by use of zinc or aluminium. The small proportion of silver contained in some copper ores is recovered in the wet extraction process by precipitation with zinc iodide. (See Ores, Cyanidation.)

The chloride volatilization process of recovering silver from ores is stated to depend for its success on the maintenance of a sufficient concentration of hydrogen chloride in the furnace, as generated by the action of silica and oxygen, or of sulphur compounds upon the salt added to the charge. The chloride thus formed is subsequently reduced to the metallic state.

Silver metal can be purified by dissolving it in nitric acid, precipitation therefrom by hydrochloric acid, and after washing the chloride thus formed, dissolving and precipitating with pure zinc. Silver can also be refined by electrolysis of its salt solutions, such as cyanide.

Silver is a white metal which is not acted upon by the oxygen of the air, but it has the property of absorbing a large amount of oxygen when in the molten state, most of which is evolved upon cooling, and is tarnished when sulphuretted hydrogen is present in moist atmosphere, due to the surface formation of silver sulphide. Silver articles deliberately coloured with sulphide are commonly but erroneously described as "oxidized" silver.

Silver is the best conductor of heat and electricity, very malleable and ductile, and, when alloyed with copper, is largely used for coinage and other purposes, also for jewellery, table-ware, and electroplating. Until recently, the British standard for coin was 92½ per cent. silver and 7½ per cent. copper, pure silver being too soft to use alone for this purpose. Silver finds considerable employment in chemical industries, vessels up to 3 or 4 cwt. being used chiefly for handling acetic acid. It is also available in thin sheet, foil, wire, tube, welded or seamless drawn, and colloidal forms. There is a stain-resisting silver alloy containing 92.5 per cent. silver which admits of soldering and is readily manipulated. (See *Silver in Industry*, by L. Addicks (Reinhold Publishing Corp., New York); and *Electroplating*.)

## SILVER, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country					Millions of Fine Ounces (1 ounce equals 480 grains or 31.1 grams)	
Germany-Austria	..	..			6.7	
Yugoslavia	..	..	..		2.3	
Czechoslovakia	..	..	..		1.0	
Sweden	..	..	..	..	1.0	
Italy	..	..	..	..	0.7	
Rumania	..	..	..	..	0.7	
					<hr/>	12.4
U.S.S.R.	..	..	..	..		7.4
Mexico	..	..	..	..	80.3	
U.S.A.	..	..	..	..	65.6	
Canada	..	..	..	..	22.8	
Honduras	..	..	..	..	3.6	
Newfoundland	..	..	..	..	1.5	
					<hr/>	173.8
Peru	..	..	..	..	19.0	
Bolivia	..	..	..	..	7.7	
Argentina	..	..	..	..	3.2	
Chile	..	..	..	..	1.5	
					<hr/>	31.4
Japan	..	..	..	..	10.0	
Burma	..	..	..	..	6.3	
Chosen	..	..	..	..	2.7	
Philippines	..	..	..	..	1.1	
					<hr/>	20.1
Belgian Congo	..	..	..	..	3.0	
Union of South Africa	..	..	..	..	1.1	
South-West Africa	..	..	..	..	0.6	
					<hr/>	4.7
Australia	..	..	..	..		14.3
Sum of above	..	..	..	..		<hr/> 264.1
WORLD PRODUCTION	..	..	..	..		270.8

**Silver Oxides** include a black monoxide ( $\text{Ag}_2\text{O}$ ) (insoluble in water), used in polishing glass, produced by the addition of an alkaline hydroxide solution to one of silver nitrate, and which, when dried and heated to  $260^\circ\text{C}$ ., gives off oxygen and is reduced to the metallic state. It is soluble in ammonium hydroxide, and the solution, on standing, deposits black shining crystals of an explosive compound known as *fulminating silver*. An oxide of the formula  $\text{Ag}_2\text{O}_2$  has been also described.

**Silver Chloride** ( $\text{AgCl}$ ) is white, insoluble in water, but soluble in ammonium hydroxide, and in sodium thiosulphate, and insoluble in hydrogen ion (acids like nitric); by the action of light it suffers slow decomposition, darkens, and loses chlorine. It is used in photography and silver-plating.

**Silver Cyanide** ( $\text{AgCN}$ ) — A white poisonous powder which decomposes when heated. It is insoluble in water, but dissolves in ammonium hydroxide, and in excess sodium or potassium cyanide. It is used in electroplating, and in medicine.

**Silver Bromide** ( $\text{AgBr}$ ) is pale yellow and less soluble than the chloride in ammonium hydroxide, but is soluble in solutions of potassium bromide and cyanide, and is used in photography.

**Silver Iodide** ( $\text{AgI}$ ) is yellowish, less soluble than the bromide in ammonium hydroxide, and is used in photography.

**Silver Nitrate** ( $\text{AgNO}_3$ ) is made by dissolving silver in dilute nitric acid, and crystallization from the evaporated solution. It is the most important soluble silver compound, as, apart from its use in photography, it is used medicinally as a caustic application, also in silver-plating, the looking-glass manufacture, and in the manufacture of an indelible ink for marking linen, etc. It is very soluble in water, crystallizes in large rhombic tables, is partially decomposed at a red heat to nitrite, giving off oxygen, and is wholly decomposed at a higher temperature, leaving the metal as a residue. "Lunar caustic" is made by melting the nitrate at about  $218^\circ\text{C}$ .

**Silver Sulphide** ( $\text{Ag}_2\text{S}$ ) is formed as a black precipitate by passing hydrogen sulphide gas through solutions of silver salts, and it occurs naturally in the form of *silver glance*. (See Argentite.) It is insoluble in water, and is used in inlaying in "niello" metal work.

**Potassium Silver Cyanide** ( $\text{KAg}(\text{CN})_2$ ) is white, crystalline, soluble in water, and used in silver-plating, etc.

**Silver "Salvarsan"** — See "Salvarsan."

**Silver Lactate** — See "Actol."

**Silver Protein (Strong Protein Silver, "Protargol")** — A loose compound of silver and protein obtained by the action of a silver compound on an alkaline solution of gelatine and containing between 7.5 and 8.5 per cent. of Ag. It occurs as a brown powder, very soluble in water, insoluble in alcohol, ether, and chloroform. It is used in medicine as a non-astringent preparation of silver for local application. It should not be confused with Mild Silver Proteinate or Silver Nucleinate ("Argyrol"), which contains between 19 and 25 per cent. of Ag and is used similarly. The descriptions "strong" and "mild"

do not refer to the silver content of these preparations. Strong protein silver is so called because it is ionized to a greater extent than mild silver proteinate and is therefore more caustic when applied to mucous surfaces.

Many silver compounds are used in photography, and the chloride, bromide, and iodide are soluble in sodium thiosulphate ("hypo"), which is extensively used for "fixing" purposes, that is, dissolving out the silver compound of the photographic plate or film that has not been decomposed by the actinic rays.

**" SILVEROID "** — A high nickel-copper alloy of great brilliancy containing 45 per cent. copper.

**SINIGRIN** — See Mustard.

**SINTER** — Incrustation on rocks, etc., deposited from springs of mineral waters.

**SINTERING** — Change in crystalline substances due to change in the size of crystals or to formation of allotropes, and formation and growth of crystals in amorphous substances. Sintering in metals and alloys is sometimes caused by the presence of small quantities of molten material between the solid parts. Sintered alumina, spinel, beryllia, zirconia, magnesia, thoria, and ceria are described by E. Ryschkewitsch in *Chem. and Ind.*, **57**, 965 (1938).

**" SIRA "** — An abrasive prepared by the formula of the British Scientific Instrument Research Association, claimed to be more rapid and economical in use than emery. (See Abrasives.)

**SISAL HEMP** is obtained from the American aloe (*Agave rigida* or *A. sisalina*) which grows in Yucatan, Mexico, Central America, and the W. Indies, and is cultivated extensively in East Africa, the chief area being in Tanganyika Territory. It is more popular with spinners than Mexican *henequen*, and is valuable for making ship's cables, twine-making, and in upholstery. It is stated, however, that the breaking-strain of sisal hawsers is inferior to that of those made from manilla hemp. (See Hemp, and Manilla.)

**61** — Element 61 is promethium (see same).

**" 666 "** — See " Gammexane."

**SIZE** — A gelatinous undried form of glue, prepared as a jelly from the third extraction of bones in the making of glue. It is largely used in common with resinous solutions and other adhesives in dyeing and calico-printing, book-binding, paper-making, etc. (See Adhesives, Glue, and Rosin Size ; for Size of Particles, see Particles.)

**SKATOLE** ( $\beta$ -Methylindole) ( $C_9H_9N$ ) — A crystalline substance, with a very unpleasant odour, of m.p.  $95^\circ C.$ , occurring in fæces and other products of putrefaction ; it also occurs in civet.

**SLAG (Dross, Scoria)** — See Iron (Slag).

**SLAG WOOL (Slagbestos)** — See Iron (Slag).

**SLATE** — A mineral form of silicate of aluminium and magnesium, a kind of argillaceous (clay-like) rock, chiefly obtained from palæozoic strata. In the forms of plates and slabs it is largely used for making school slates and roofing. In a finely pulverized flour-like form it is used as a "filler" of inert character, also in compounding preparations of rubber, paints, pencils, floor-covering compositions, paper, asphaltic mixtures, and so forth.

**SLIP** — See Porcelain.

**SLUDGES** — See Sewage.

**SLUSH CASTING** — A technique whereby molten metal is dumped out of a mould after partial solidification has occurred along the mould surface. This process is employed in the casting of metal statuary and some toys.

**SMALT** — See Cobalt.

**SMALTINE (Smaltite)**, (crystal system No. 1, and sp. gr. 6.5 to 7.2) — See Cobalt.

**SMELTING** — Metallurgical operation in which the metal is separated in a state of fusion from the impurities with which it may be chemically or physically associated in the ore. (See Metallurgy, and Ores.)

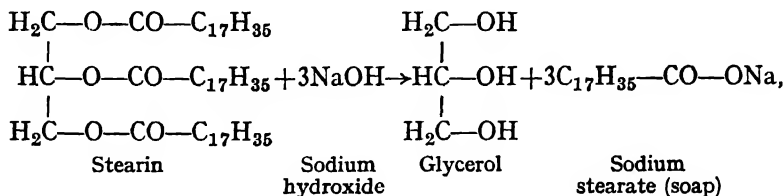
**SMITHSONITE** — Mineral silicate of zinc,  $2\text{ZnO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ , of crystal system No. 4, and sp. gr. 3.16 to 3.50. (See Zinc.)

**SMOKE** arises from imperfect combustion of fuel in domestic grates, boiler furnaces, brick kilns, and in certain process operations; that from domestic grates and boiler furnaces containing more or less tarry substances and soot. The thick dark fogs of London and other industrial areas are largely due to the condensation of water on smoke particles. The annual solids falling in the London area amount to about 460 tons per square mile. (See *The Smoke Problem of Great Cities*, by N. F. Shaw and J. S. Owens (Constable and Co., London); *Smoke: a Study of Town Air*, by J. B. Cohen and A. G. Ruston (E. Arnold and Co., London); *Clouds and Smoke*, by W. E. Gibbs (J. and A. Churchill, London); report of discussion on "Smoke Abatement in Industry" in *Chem. and Ind.*, 51, 429 (1932); *Smoke: A Study of Aerial Disperse Systems*, by R. Whytlaw-Gray (Edward Arnold and Co., London); and the Reports of the Advisory Committee of Atmospheric Pollution (H.M. Stationery Office); also Aerosols, Air, Dusts, Fogs, Gases, and Mists.)

Smoke clouds, or smoke screens, are intentionally produced by burning of phosphorus in air forming white smoke of phosphorus pentoxide; by discharging titanium tetrachloride into air, whereupon the moisture in the air produces white smoke of titanate acid; or by incomplete combustion, especially of oil fuel, producing black smoke, all of which forms of smoke may be produced in such a way as to purposely obscure objects.

**SMOKELESS FUELS** — See Fuel (Smokeless).

**SOAPS and DETERGENTS** — **Hard Soaps** are made from the harder fats, such as tallow, mutton fat, palm, palm kernel, coconut, cotton-seed, soy-bean, and hydrogenated oils, etc., with or without the addition of from 5 to 10 per cent. rosin (which also combines with alkali) by boiling with caustic soda lye (sodium hydroxide) of sp. gr. 1.05, the soap, after decolorization with sodium hyposulphite (if necessary), being afterwards "salted" out by the addition of common salt, which renders it insoluble. This action of salt in graining-out soap consists of its conversion into fibres, etc., of a comparatively low degree of hydration. 1,000 pounds of fat yield about 2,000 pounds of soap lye containing about 5 per cent. glycerol and 10 per cent. mineral salts. A typical reaction is that of stearin, thus :



After withdrawing the spent lye, from which glycerol (glycerine) is obtained, the soap is solidified in rectangular iron frames or "soap coolers," hardened (dried) by keeping, and then cut up into slabs and bars by means of wires. It has been shown by microscopic examination that most soaps are built up of anisotropic constituents, that is, crystals, crystalline fluids, viscous fluids, syrup, fibres, solutions, and (sometimes) gels. An investigation by McBain and Hay supports the conception that soap solutions are crystalloidal when sufficiently dilute, and colloidal in higher concentration.

The "Autoclave" process and "Twitchell" process for fat splitting, etc., are described under the heading of Fats.

Attempts have been made, with more or less success, to introduce colloidal clay (made from china clay) into soaps to the extent of from 15 to 20 per cent., and claims have been made that some of the products exhibit superior lathering and detergent properties as compared with soaps devoid of this material. The use of even 5 per cent. rosin will impart a perceptible yellow tint to white goods washed with soap containing that amount, but it possesses the advantage of giving the soap a firmer consistence.

Soap solutions possess a high degree of electrical conductivity in dilute or concentrated solution.

There is a process of washing that consists in immersing the fabrics in a dilute aqueous emulsion of fatty acids (preferably olein), the emulsion being stabilized by addition of turkey-red oil or other suitable material and treatment of the impregnated material with dilute alkali, preferably sodium carbonate, thus generating the soap *in situ*.

The use of hydrogenated phenols (secondary alcohols of cycloparaffin hydrocarbons) for increasing the cleansing power of soaps is referred

to elsewhere. (See "Hexalin," Hydrogenation, and Hydrogenated Phenols.)

**Castile Soap** is a hard soap used for making pills and plasters, made from olive oil and caustic soda.

**Silicated Soaps** are otherwise ordinary soaps into which a proportion of an alkaline silicate is introduced, as these substances, like true soaps, have the property of liberating alkali when dissolved in water. The statement has been made that silicate is not a detergent *per se*, but that it functions as such with greasy substances. The introduction of silicate, however, permits of the use of oils which melt at low temperature, and thus yields soap containing a large proportion of sodium oleate, which will not dissolve too readily in use. It also improves the emulsifying power, so that altogether sodium silicate is not a mere filler or adulterant; moreover, soaps containing silicate are not so liable to "bloom."

**Ethanolamine Soaps** are combinations of fatty acids and certain organic bases that are derivatives of ammonia in which its hydrogen atoms are more or less or entirely replaced by the ethanol residue,  $-\text{CH}_2\text{CH}_2\text{OH}$ . The triethanolamine salts of the fatty acids are purely organic soaps, and yield precipitates with acids and with hard water, but have the advantage of being soluble in organic solvents and hence are used in dry-cleaning.

**Sulphated Alcohol Detergents** are not soaps, but perform the cleansing function associated with the ordinary use of soaps. They are made by hydrolysis of the fats, followed by hydrogenation if required, and treatment of the long-chain fatty acids (produced in this way) with sulphuric acid to form sulphated alcohols, the sodium salts of which are effective detergents, such as "Gardinol," "Orvus," "Igepon," "Dreft," "Drene," "Modinal," etc. Unlike true soaps these are stable in acid solutions, and in hard water they produce no precipitates, as their calcium and magnesium salts are soluble. For these reasons they are popular as "soapless shampoos."

**Mottled Soaps** are produced by adding to the nearly finished hard soap mass crude soda liquor containing some sodium sulphide, from a watering-pot. In this way, any iron that may be present in the soap combines with the sulphur of the sulphide to form iron sulphide, which makes its appearance in streaks or veins. In some cases a little ferrous sulphate is added to the soap during the boiling, and this forms ferric oxide, thus mottling the soap in a marked degree. Again, in other cases "mottling" is produced by the addition of Prussian blue or ultramarine. The practice serves no useful purpose.

**Soft Soaps** are made chiefly from linseed, castor, cotton, and other seed and fish oils, tallow or resin being at times incorporated in certain proportions for stiffening purposes, while potash lye (potassium hydroxide) is used as the saponifying agent. Potash lye, however, is not indispensable, as good soft soap can be made by the use of mixed olein stock, resin, and caustic soda. In some cases the glycerol is left in the soap, which is heated and stirred until it "talks," during which operation much of the water is evaporated, after which it is ready for

packing. In other cases the glycerol is removed from the soap by chemical processes. (See Glycerol.)

**Toilet Soaps** are made of hard soap of various qualities, perfumed or impregnated with mild essential oils, or any other suitable materials, such as terpineol, bromostyrol, benzaldehyde, benzyl acetate, diphenylmethane, etc., appropriately dried, sometimes milled and ribboned, and then suitably moulded into tablets. An ideal fat base for toilet soap is stated to be made of 80 per cent. tallow and 20 per cent. coconut oil. The transparent character of certain varieties is obtained by the addition of sugar, honey, or alcohol, while opacity can be obtained by the incorporation of  $\frac{1}{2}$  per cent. zinc oxide. Among colouring materials used for toilet soap may be mentioned Rhodamine B, Xylene Blue, and Tartrazine.

**Textile Soaps** should not contain above 30 per cent. water, 1 per cent. free sodium carbonate, and be devoid of caustic soda, silicate, and rosin.

**Metallic Soaps** include the stearates, palmitates, and oleates of aluminium, ammonium, antimony, arsenic, barium, bismuth, cadmium, calcium, chromium, cobalt, copper, iron (ferrous and ferric), lead, lithium, magnesium, mercury (mercurous and mercuric), silver, strontium, tin, and zinc, many of which are used industrially in waterproofing processes; some as vehicles for medicinal salves, plasters, and ointments; also in making lubricating and fungicidal preparations, anti-fouling paint and varnish driers, and in laundering and dry cleaning.

Their successful use in most cases depends on their colloidal condition, and fats such as lanolin and beeswax have a stabilizing effect on colloidal metallic soap solutions. Heat, dry air, and ultra-violet rays tend to destroy their colloidal state, and reduce them to a dusty condition. Their waterproofing value is due to their capability of absorbing water, thus swelling up and filling the pores of the subject material. The aluminium, magnesium, and calcium soaps of the stearic series are stated to be superior as heat-proofing insulating materials.

**Soap Films** — Films and bubbles when first formed are thick and colourless. In his book on *Soap Films* (G. Bell and Sons, Ltd., London), A. S. C. Lawrence states that "the fundamental change is the thinning (which at first produces the pink and green bands, and all the purer colours of Newton's scale which gradually disappear on further thinning), and this process ultimately results in the formation of the so-called 'black spot.'" He concludes that the "critical fall consists of a gradual breakdown of one of the surface layers; coalescence of the liquid film on the remaining surface layer following as a matter of course." Black appears at a number of points and spreads all over the film as the thinnest possible film and the only stable one.

Many factors, such as wetting, lubrication, deflocculation, lathering, and solution, are involved in the **detergent action** of soap. Thus, the surface tension of water is lowered from, say, 72 dynes per centimetre to 30 by the presence of 0.05 per cent. of soap. This facilitates the emulsification of oils, fats, and greases, and also allows the solution to

penetrate better into materials of open structure such as textiles, thus making it possible to readily remove foreign matter (dirt) by rinsing with water.

See J. K. Rowe on "The Hydrolysis of Fats" (*J.S.C.I.*, **52**, 49 T (1933)); E. L. Smith on "The Kinetics of Soap Making" (*J.S.C.I.*, **51**, 337 T (1932)); "The New Detergents," by R. A. Duncan (*Ind. Eng. Chem.*, **26**, 24 (1934)); "The Preparation of Anhydrous Metallic Soaps," by L. W. Ryan and W. W. Pelchner (*Ind. Eng. Chem.*, **26**, 909 (1934)); "Mechanism of Fat-Splitting," by L. Lascaray (*Ind. Eng. Chem.*, **41**, 786 (1949)); *The Modern Soap and Detergent Industry*, by G. Martin and E. I. Cooke (Technical Press, Surrey); *Soap and Glycerine Manufacture*, by E. T. Webb (Davis Bros., London); *Colloid Science*, by James W. McBain (D. C. Heath and Co., Boston); Esters, and Fats.

**SOAP BARK** — See Quillaya.

**SOAP-STONE** ( $\text{H}_2\text{Mg}_3\text{Si}_4\text{O}_{12}$ ) — A massive variety of talc, being a hydrous silicate of magnesia, largely used in the form of sawn blocks and bricks for building the furnaces used in the method of recovery of the alkali from sulphate paper-mills in Canada, etc. (See French Chalk, Steatite, and Talc.)

**SOBREROL (Pinol Hydrate)** ( $\text{C}_{10}\text{H}_{16}(\text{OH})_2$ ) — A crystalline compound formed from pinene by the action of moist air and sunlight; m.p.  $150^\circ\text{C}$ . (See Pinene.)

**SODA** — See Sodium (Carbonate).

**SODA ALUM** — See Aluminium (Alums).

**SODA ASH** — Crude sodium carbonate. (See Sodium (Carbonate).)

**SODA LIME** — A reagent used in making nitrogen determinations in organic analyses; also for the absorption of various acid gases, such as phosgene, in military operations. It consists of caustic soda and quicklime, and is made by moistening a mixture of the two ingredients with a solution of caustic soda, drying the mixture, and grading the sizes of the resulting lumps. (See "Sofnol.")

**SODAMIDE** ( $\text{NaNH}_2$ ) is obtained by passing dry ammonia gas over molten sodium at  $300^\circ\text{C}$ . in the absence of air. It melts at  $155^\circ\text{C}$ ., is decomposed by water, and finds use as a powerful dehydrating agent in processes for the synthetic production of indigo from aniline and the manufacture of sodium cyanide.

**SODA NITRE** — See Caliche, and Sodium (Nitrate).

**"SODA OLEIN"** — See Turkey-Red Oil.

**SODIUM (Na) and its Compounds** — Atomic weight, 22.997. See Elements for other data. The Siberian lake Petuchow is stated to contain large quantities of sodium carbonate, and at Lake Magadi in British East Africa there exists a vast and remarkable deposit of natural crystalline sesquicarbonate of soda, estimated at 200,000,000 tons of soda (free from sulphur impurities). It is stated to contain sodium salts to the extent of 40.38 per cent. calculated as  $\text{Na}_2\text{O}$ , and this upon

the calcined product amounts to 58.08 per cent., or 99.3 per cent. dry soda ash ( $\text{Na}_2\text{CO}_3$ ). (See Magadi Soda.)

The chloride (common salt,  $\text{NaCl}$ ) is a constituent of sea-water, which contains an average of about 28 parts per 1,000. Salt also occurs naturally in large deposits in Cheshire, Lancashire, Worcestershire, Poland, New York, Michigan, West Virginia, Louisiana of the United States, Saskatchewan (Canada), some lakes in China, Great Salt Lake (Utah), the Dead Sea, and elsewhere. In the areas of Winsford and Northwich there are two layers of salt separated by about 30 feet of hard marl, each of about 80 feet thickness, the top one occurring at a depth of 120 to 130 feet below the surface.

The nitrate ( $\text{NaNO}_3$ ) is the principal constituent of *caliche* or *soda nitre*, which is found in large quantities in Chile and Peru. (See Caliche.)

**Metallic Sodium** is now made in large quantity by the electrolysis of fused caustic soda at a temperature of about  $20^\circ\text{C}$ . above its melting-point, and by the electrolysis of fused sodium chloride, using a cathode of molten lead, and subsequent electrolysis of the resulting sodium-lead alloy in fused sodium hydroxide. In the electrolysis of caustic soda, metallic sodium and hydrogen are liberated at the cathode and oxygen at the anode, and in the case of the chloride chlorine is liberated at the anode.

It is a light, soft, silver-like metal, and on account of its ready oxidizability has to be preserved in kerosene or naphtha, although it is not affected by perfectly dry air or oxygen. Metallic sodium is very like potassium in most respects and decomposes water with considerable violence on being thrown into it, forming sodium hydroxide or caustic soda ( $\text{NaOH}$ ) solution. It is used as for reducing, dehydrating, polymerizing, decolorizing, deodorizing, dehalogenating, condensing in many organic reactions, and in the manufacture of lead tetraethyl. Some use of the metal has been made in alloys, in the liquid-phase as a heat-transfer medium, and as a scavenger agent for metals. Colloidal sodium is available in numerous organic substances.

**Sodium Amalgam** can be prepared by heating mercury to  $200^\circ\text{C}$ ., and adding sodium in small pieces slowly, or by melting sodium under a layer of toluene and adding mercury slowly to the melted sodium. Various grades may be made containing sodium from 2 to 10 per cent., and are useful as reducing agents, also for the preparation of hydrogen.

**Sodium-Lead Alloy** (Du Pont) — A homogeneous alloy containing 2 per cent. sodium. Used as a deoxidizer and homogenizer in the casting of non-ferrous alloys having lead as the principal constituent.

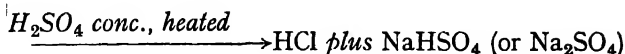
**Sodium-Zinc Alloy** (Du Pont) — A homogeneous alloy containing 2 per cent. sodium. Used as a deoxidizer and homogenizer in the casting of non-ferrous alloys having zinc as the principal constituent.

**Sodium Chloride**, from sea-water (in association with the other saline constituents), is obtained in Turks Island (British Caicos group) and other Eastern parts in an impure, coarse form by the evaporation of the water in shallow cavities on sea-beaches, the product being known as "solar salt," and used for fish-curing. Salt is similarly recovered by solar evaporation in a large way at San Francisco Bay, Great Salt Lake, Cette (France), and the Dead Sea. (See Brine.)

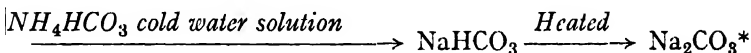
SODIUM CHLORIDE, CHART SHOWING PRINCIPAL APPLICATIONS  
OF MANUFACTURE

Arranged by the Editor.

NaCl



$$\xrightarrow{\text{Electrolysis of water solution}}$$


$$\xrightarrow{\text{Electrolysis of fused salt}}$$


\* By the action of acids practically all their corresponding sodium salts are formed.

Mining of salt in Cheshire has been practically superseded by brine pumping and evaporation, as this method separates insoluble impurities and gives ease of transport. By varying the temperature of evaporation and by supplying suitable additional agents, salt is produced to suit various industrial demands in the respective forms of "fishery" salt of coarse grain, "bay" salt of still coarser grain, and "butter" salt of fine soft grain. Meat canners require it in finely granulated form, and flour millers in even more finely ground condition. In table salt 1 per cent. of a filler is added to prevent caking.

Sodium chloride melts at 804° C., is very soluble in water, and, apart from the enormous quantities used in the alkali trade, it is largely used for "salting" out soaps; also as a food preservative, fertilizer, in the ceramic industries, in dyeing and calico-printing, glazing earthenware and firebricks, etc.

Rock salt (crystal system No. 1) varies in composition according to the extent of admixed marl, but contains on average about 95 per cent. of chloride, and, as such, is used for preserving hides and for feeding live-stocks, etc.

"Vacuum" salt is made by boiling brine under vacuum as distinct from "pan" salt made by diffusive evaporation, and consists of small uniform crystals of solid pure character, being practically free from mother-liquor, whereas the "pan" crystals, being partially hollow, contain some mother-liquor. Vacuum pans are generally run in connection with power plants, the exhaust steam being used for effecting evaporation. (See *Technology of Salt Making in the United States*, U.S. Bur. of Mines. Bull. 146, 1917.)

## SODIUM

## SALT (SODIUM CHLORIDE), WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country					Salt Millions of Metric Tons
Germany	..	..	..	..	3.5
United Kingdom	..	..	..	..	3.0
France	..	..	..	..	2.2
Italy	..	..	..	..	1.5
Poland	..	..	..	..	0.6
Spain	..	..	..	..	0.5
Rumania	..	..	..	..	0.3
Czechoslovakia	..	..	..	..	0.2
					<hr/> 11.8
U.S.S.R.	..	..	..	..	4.5*
U.S.A.	..	..	..	..	8.0
Canada	..	..	..	..	0.4
					<hr/> 8.4
Brazil	..	..	..	..	0.7
Argentina	..	..	..	..	0.3
					<hr/> 1.0
China	..	..	..	..	3.0
British India	..	..	..	..	1.6
Japan	..	..	..	..	0.7*
Aden	..	..	..	..	0.3
Korea	..	..	..	..	0.2
Turkey	..	..	..	..	0.2
Indochina	..	..	..	..	0.2
					<hr/> 6.2
Egypt	..	..	..	..	0.3
					<hr/> 32.2
Sum of above	..	..	..	..	
WORLD PRODUCTION	..	..	..	..	34.0*

\* Estimated.

**Sodium Hydroxide (Caustic Soda)** ( $\text{NaOH}$ ) (m.p.  $318^\circ \text{C.}$ ) is largely manufactured for use in many chemical applications, especially in the making of soap, being capable of decomposing fats and oils, thus liberating glycerol, and of combining with the fatty acids simultaneously produced. (See Soaps.)

Caustic soda is made by treatment of sodium carbonate solution with lime, the liquors being thus "causticized" and attended with the production of calcium carbonate as a by-product. After separation

from the insoluble calcium carbonate, the liquor is either evaporated down to a strength of 90° Tw. for soap-making or further to a state of fusion. About one-fourth of the caustic soda used in the United States is made in this way, much of it in the establishment where it is used, for example, paper-pulp factories.

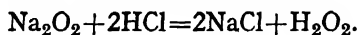
There are a number of cells used in the electrolytic process, including the "Castner-Kellner" mercury type, the "Bell" type (used in Australia), the "Allen-Moore," the "Townsend," the "Nelson," the "Hooker," the "Wheeler," the fused electrolyte type, and the "Gibbs diaphragm" type. The efficiency of the various cells varies greatly according to the different operating conditions; the diaphragm type seems to be prevailing.

The first essential is the use of a saturated solution of sodium chloride devoid as far as possible of impurities. The products in each case are identical, namely, chlorine, hydrogen, and caustic soda. The greater the concentration of OH ions, the more the chlorine liberated unites with them to form hypochlorous acid and (eventually) sodium hypochlorite. As the electrolysis proceeds OH ions carry increasingly more and more of the current, so that a limit is economically reached at which the liquor must be withdrawn from the cell, and the contained sodium chloride recovered by fractional crystallization. The favourite type of evaporator is that which works under vacuum, heated by exhaust steam from power plant; weak liquor from the cells can thus be concentrated to about 1.45 sp. gr., and on cooling and settling in large tanks the salt settles out, and a clear, fairly pure liquor is run off, to be further concentrated in finishing pots and solidified. It is understood that a decomposition efficiency of about 50 per cent. is most economical. The chlorine generated in electrolytic processes as above described can be utilized in the manufacture of bleaching-powder or condensed and liquefied. A solution of sodium sulphate in water of 40 per cent. strength can by electrolysis be resolved to a large extent into caustic soda and sulphuric acid.

Caustic soda is a white, highly deliquescent, caustic substance, and is marketed in several forms—"ground," "flake," "detached," "pellets," and "stick"—and of varying degrees of purity and strength, suited to its several applications. These also include a practically pure variety in liquor form of 90° Tw. strength; solid forms of from 60 to 76 per cent. (in terms of  $\text{Na}_2\text{O}$ ); powder form of from 77 to 78 per cent. (in terms of  $\text{Na}_2\text{O}$ ); and a crude form containing from 40 to 42 per cent. (in terms of  $\text{Na}_2\text{O}$ ). (For the conversion of data "in terms of  $\text{Na}_2\text{O}$ " into percentage of actual NaOH, the ratio 62:80 must be applied, that is, 62 per cent. in terms of  $\text{Na}_2\text{O}$  is the same as 80 per cent. of NaOH.)

**Sodium Oxides**—Sodium monoxide ( $\text{Na}_2\text{O}$ ) is a white amorphous body produced from the metal when partially oxidized by a limited supply of oxygen, the excess of metal being subsequently distilled off *in vacuo*. Sodium oxide has been commercially available since 1934, with the advantage of 22.5 per cent. by weight in its favour over sodium hydroxide.

Sodium peroxide ( $\text{Na}_2\text{O}_2$ ) results from the burning of metallic sodium in oxygen, and is commercially made by passing purified dry air over metallic sodium placed on trays of aluminium at a temperature of  $300^\circ\text{C}$ . It is a nearly white substance of considerable commercial importance, owing to the fact that in contact with water or dilute acids it decomposes, yielding hydrogen peroxide in solution :



It is consequently used as a bleaching agent for wool, silk, yarn, and various fibres, also in refining oil and fats, and in the straw-hat, wood pulp, and other industries. Exposed to the air in contact with combustible materials it constitutes a dangerous material, owing to the heat developed by its decomposition with moisture. Trade-mark is "Solozone" (Du Pont).

**Sodium Carbonate (Soda Ash)** ( $\text{Na}_2\text{CO}_3$ ) — Sodium carbonate is extensively used in glass manufacture, and is the basis of "washing-soda" (soda crystals) ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ), which is largely employed for cleansing purposes. In its several commercial forms it is obtained from common salt by a number of chemical processes.

When common salt ( $\text{NaCl}$ ) is subjected to the action of strong sulphuric acid at an elevated temperature, the interaction produces sodium sulphate (salt-cake) and hydrochloric acid gas, which latter substance can be subsequently condensed and dissolved in water. By the old superseded Leblanc process, crude sodium carbonate was made by furnacing sodium sulphate (produced as above described) with chalk or limestone or lime and small coal, calcium sulphide being formed together with the sodium carbonate. The latter substances were then leached out of the mass, and the solution evaporated. The recovery of sulphur from the calcium sulphide of alkali waste by the Chance process is described under the heading of Sulphur.

The heating of sodium bicarbonate (see same) is the principal method used to manufacture sodium carbonate.

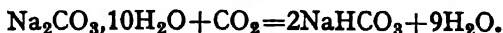
Soda crystals ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) effloresce or give up water when exposed to the air, the crystals falling to powder having the composition  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . Another form can be obtained in rhombic crystals by crystallization from hot solutions, with the composition  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ . Soda ash is the dehydrated carbonate,  $\text{Na}_2\text{CO}_3$ .

In addition to the pure anhydrous state, sodium carbonate is marketed in crystal form, and also as so-called "soda-ash" of 58 per cent. (in terms of  $\text{Na}_2\text{O}$ ) strength. (For the conversion of data "in terms of  $\text{Na}_2\text{O}$ " into percentage of actual  $\text{Na}_2\text{CO}_3$ , the ratio 62 : 106 must be applied, that is, 55.8 per cent. in terms of  $\text{Na}_2\text{O}$  is the same as 95.4 per cent. of  $\text{Na}_2\text{CO}_3$ .)

Apart from the uses of sodium carbonate already noted, it is largely employed in ceramics and paper-making, the manufacture of soaps, wool-scouring, metallurgy, as a flux, and in the leather trade.

*References:* *Manufacture of Soda*, by Te-Pang Hou (Reinhold Publishing Corp., New York) ; *The Alkali Industry*, by J. R. Partington (Baillière, Tindall and Cox, London ; D. Van Nostrand Co., New York).

**Sodium Bicarbonate** ( $\text{NaHCO}_3$ ) — Sodium hydrogen carbonate or sodium acid carbonate or sodium bicarbonate is obtained commercially by the ammonia-soda process referred to below, but can be made by the action of carbon dioxide upon the ordinary carbonate :



Sodium carbonate and bicarbonate deposits occur naturally in British Columbia, where they are used in soap-making. There is also a so-called sesquicarbonate of sodium, named *trona* ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ), (see same).

In the ammonia-soda process, sodium chloride and ammonium hydrogen carbonate (ammonium bicarbonate) are made to interact in such a way as to result in the formation of ammonium chloride and hydrogen sodium carbonate :  $(\text{NH}_4)\text{HCO}_3 + \text{NaCl} = \text{NaHCO}_3 + \text{NH}_4\text{Cl}$ . A brine solution is saturated with ammonia gas, and the liquid is then charged with carbon dioxide gas and the solution maintained at 26 to 27° C. while the sodium bicarbonate crystallizes out. This can be converted into the normal carbonate by calcination. The ammonium chloride, which is more soluble, remains in solution, and the ammonia is afterwards recovered from it by the action of lime, giving calcium chloride as a by-product :  $2\text{NH}_4\text{Cl} + \text{Ca}(\text{OH})_2 = \text{CaCl}_2 + 2\text{NH}_3 + 2\text{H}_2\text{O}$ . The calcium chloride, by treatment with zinc oxide and carbon dioxide under pressure, produces zinc chloride and calcium carbonate, which can be used again to produce carbon dioxide, and the zinc chloride can be electrolysed, producing electrolytic zinc and chlorine. (See E. N. Trump on "Looking Back at 50 Years in the Ammonia-Soda Alkali Industry" (*Chemical and Metallurgical Engineering*, 40, 126 (1933)).)

Sodium bicarbonate is largely used in compounding effervescent salts, artificial mineral waters, baking-powders, and in the textile, tanning, paper, ceramic, and other industries.

**Sodium Percarbonate** ( $\text{Na}_2\text{C}_2\text{O}_6$ ) — A compound described under this name is said to be more suitable than sodium peroxide ( $\text{Na}_2\text{O}_2$ ) as a bleaching agent for fabrics. (See Bleaching.)

**Sodium Sulphate** ( $\text{Na}_2\text{SO}_4$ ), known commercially as Glauber's salt ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) and "salt-cake," is found naturally as the mineral *thenardite*, whilst *glauberite*, of which many deposits are found, is a double sulphate of sodium and calcium. There are also a number of deposits of sodium sulphate in Canadian lakes, one of which (Muskiki Lake) is worked near Dana, and another at Frederick Lake, being used for conversion into acid sodium sulphate for the separation of copper and nickel.

Apart from its incidental production in various processes, it is obtained from Stassfurt salts by interaction between magnesium sulphate and sodium chloride :  $2\text{NaCl} + \text{MgSO}_4 = \text{Na}_2\text{SO}_4 + \text{MgCl}_2$ . It is a soluble substance, which crystallizes with 7 and 10 molecules of water ( $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) respectively. These melt in their own water of crystallization when heated to 33° C., and in ordinary atmospheres are efflorescent, losing all the water of crystallization, and becoming what is known as "desiccated Glauber's salt." It has

medicinal value as a purgative, and finds many uses, particularly in glass-making, nickel refining, and dyeing, while it is also of importance as the starting material for the manufacture of sodium sulphide.

By electrolysis under suitable conditions, a solution of the sulphate yields caustic soda at the cathode and sulphuric acid at the anode.

A review of the world's supplies is given by H. O. Moraw (*C.T.J.*, **87**, 157, 202 (1930)) ; and " Dehydration of Natural Occurring Sodium Sulphate Crystals at Horseshoe Lake, Sask." is presented by James B. Pierce, Jr., in *Transactions of the American Institute of Chemical Engineers*, **34**, 153 (1938).

**Sodium Hydrogen Sulphate** ( $\text{NaHSO}_4$ ), known also as " bisulphate," acid sodium sulphate, and " nitre-cake," was produced on an immense scale during World War I as a by-product in the manufacture of nitric acid which is generally not pushed beyond the first state, as represented by the equation  $\text{NaNO}_3 + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HNO}_3$ . It became a matter of considerable importance to devise means of utilizing this residual substance containing the equivalent of a mixture of 30 per cent. sulphuric acid and 70 per cent. of sodium sulphate. In one of these methods, ammonia gas was passed into a heated solution of the nitre-cake containing a proportion of sulphuric acid, and after saturation, the bulk of the sodium sulphate thus produced was crystallized out, leaving ammonium sulphate in the mother-liquor, from which it was obtained by crystallization or evaporation to dryness. The reaction :  $2\text{NaHSO}_4 + 2\text{NH}_3 = \text{Na}_2\text{SO}_4 + (\text{NH}_4)_2\text{SO}_4$ .

In another method " Gafsa " phosphate is dissolved in a solution of nitre-cake, 100 parts of the phosphate (59 per cent. strength) requiring about 184 parts of the nitre-cake to furnish the required amount of  $\text{SO}_3$  ; 44.63 parts of water being used and subsequently increased by a further 10 per cent. The product thus obtained is used as a fertilizer.

Nitre-cake can be utilized to generate fuming sulphuric acid by dry distillation. Nitre-cake may be used in grease recovery, bleaching and dyeing, metal pickling, hydrochloric acid manufacture, mineral water making, and as a flux in decomposition of certain minerals.

**Sodium Persulphate** ( $\text{Na}_2\text{S}_2\text{O}_8$ ) is prepared like the corresponding potassium salt, namely, by electrolysis of a solution of sodium hydrogen sulphate in a divided cell, and finds use in the preparation of strong hydrogen peroxide. It is stated to be non-explosive.

**Sodium Aluminium Sulphate** (Soda Alum) — See Aluminium (Alums).

**Sodium Sulphites** are referred to under Sulphur (Sulphurous Acid). They are used commercially on account of their value in the brewing industry and as bleaching agents. The bisulphite powder ( $\text{NaHSO}_3$ ) used in the brewing trade has a value in terms of  $\text{SO}_2$  (sulphur dioxide—upon the basis of which it is sold) of from 60 to 67 per cent., and it is also prepared in liquid form of 70° Tw. strength yielding about 25 per cent.  $\text{SO}_2$  in use.

**Sodium Hydrosulphite** ( $\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) is a yellowish-white crystalline substance, soluble in water, used as a bleaching and reducing agent. It is made by dissolving zinc in sodium bisulphite and precipitation with milk of lime, leaving the sodium hydrosulphite in solution. The water

of crystallization can be removed from the salt by hot alcohol. (See Hydrosulphites, and "Hydros.")

**Sodium Thiosulphate** ( $\text{Na}_2\text{S}_2\text{O}_3$ ) (Incorrectly "Hyposulphite") — See Sulphur (Compounds).

**Sodium Sulphide** ( $\text{Na}_2\text{S}$ ) is a reddish-yellow compound soluble in water, prepared for commercial purposes in crystalline form containing 30 to 33 per cent., and in a fused form of 60 to 65 per cent. strength. It is commonly made from the sulphate by heating with coal slack or coke at a low temperature in a rotary fuel-fired furnace. This gives a low yield and slow production, whilst a high temperature gives rapid production and corrosive destruction of the furnace. As thus made, when crystallized from aqueous solution, it contains 9 molecules of water and 32.5 per cent.  $\text{Na}_2\text{S}$ , and upon further evaporation and continued heating up to  $160^\circ\text{C}$ . a final product is obtained containing 60 to 65 per cent.  $\text{Na}_2\text{S}$  which is cast into slabs. It can also be made by the action of hydrogen sulphide upon caustic soda, and is a by-product in making barium carbonate by treatment of barium sulphide with sodium carbonate.

Sodium sulphide is used for denitrating artificial silk, for decomposing silver iodide (as a substitute for the "Claud t" process), for separating gold and silver from tower-acid liquors, in the manufacture of sulphur dyes, in the paper-making industry ("sulphate" pulp), and as a depilatory in tanning, etc. (See "Manufacture of Sodium Sulfide," by J. F. M. White and A. H. White (*Ind. Eng. Chem.*, **28**, 244 (1936)).) Sodium sulphide will flux all refractories. There are other sulphides corresponding to the potassium sulphides, and all can be used as depilatory agents and in the manufacture of black sulphur dyes.

Other sodium compounds are arranged here alphabetically by their principal element, except that those containing carbon (sodium-organic compounds) are also alphabetically arranged immediately following the present listing.

**Sodium Aluminate** ( $\text{NaAlO}_2$ ) is a white compound soluble in water, resulting from the fusion of bauxite or precipitated aluminium hydroxide with sodium carbonate; used as a mordant and water softener for boiler water.

**Sodium Arsenates** are isomorphous with the phosphates and include the following well-known salts: trisodium orthoarsenate (or normal arsenate),  $\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$ , a salt which is commercially known as arseniate, marketed of 45 per cent. strength, and used as an anti-septic, also in dyeing, in medicine, and as a fungicide; disodium hydrogen orthoarsenate,  $\text{Na}_2\text{HAsO}_4$ , largely used in calico-printing; sodium dihydrogen orthoarsenate,  $\text{NaH}_2\text{AsO}_4$ ; sodium pyroarsenate,  $\text{Na}_4\text{As}_2\text{O}_7$ ; and sodium metarsenate,  $\text{NaAsO}_3$ .

**Sodium Arsenite** ( $\text{Na}_2\text{HAsO}_3$ ) is a white compound, soluble in water; used in making arsenical soap for taxidermists, in dyeing, and as a weed killer.

**Sodium Borate** — See Boron (Compounds).

**Sodium Perborate** ( $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ ) is a colourless, crystalline salt prepared by mixing a 3 per cent. solution of hydrogen peroxide with a

saturated solution of borax in alkaline solution at a low temperature, when it is deposited in crystalline form on standing. It is produced electrolytically from a solution of sodium carbonate and borax. Another patented method is based upon the interaction of sodium peroxide and sodium metaborate, the first-named salt being dissolved in cold water and the cold solution saturated with carbon dioxide, then mixed with a saturated solution of the metaborate. The sodium perborate which crystallizes out is separated by filtration and dried. It is a dangerous substance, liable to decompose with violence, although stated to be stable in air kept free from carbon dioxide. It contains 10.4 per cent. of oxygen, and is used in compounding preparations for washing and bleaching textile fabrics and as a general oxidizing agent. Proprietary brands are sold as "Clarax" and "Ozonite."

**Sodium Bromide** (NaBr) and **Iodide** (NaI), both of which are used in photography and medicine, are readily soluble in water and are white crystalline salts produced by processes like those used for preparing the corresponding potassium compounds. The iodide is also employed as a solvent of iodine, and to some extent in the wet extraction of silver.

**Sodium Chlorate** ( $\text{NaClO}_3$ ) and **Perchlorate** ( $\text{NaClO}_4$ ) are white crystalline salts, soluble in water, prepared much in the same way as the potassium compounds, and used for the same purposes. The chlorate finds use in calico-printing processes, for destroying weeds, and, being more soluble than the potassium salt, is preferred for making aniline black. Since sodium chlorate is a strong supporter of combustion its use is accompanied by considerable hazard in the presence of combustible materials such as clothes, hay, and wood.

**Sodium Chlorite** ( $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$ ), prepared from barium chlorite and sodium sulphate, forms lustrous laminæ, and in the anhydrous form explodes on percussion. It is also made by reaction of sodium peroxide and chlorine dioxide (explosive) thus:  $\text{Na}_2\text{O}_2 + 2\text{ClO}_2 \rightarrow 2\text{NaClO}_2 + \text{O}_2$ . In dyeing with vat or sulphur dyes the leuco (colourless) compounds (formed by the use of sodium hydrosulphite or sodium sulphide) are readily absorbed by cotton fibres, and are then restored to their original colours by oxidizing treatment with sodium dichromate or sodium chlorite. The chlorite has the advantage of forming sodium chloride, colourless and easily removed by washing.

**Sodium Hypochlorite** ( $\text{NaOCl}$ ) — See Chlorine (Compounds).

**Sodium Chromate** and **Sodium Dichromate** — See Chromium (Compounds).

**Sodium Fluoride** (NaF) is a white crystalline salt soluble in 25 parts of water, and the solution, which attacks glass, is used in etching, also as an insecticide, and for other applications. It is prepared by neutralizing hydrofluoric acid with sodium carbonate.

**Sodium Fluosilicate** ( $\text{Na}_2\text{SiF}_6$ ), also named silicofluoride, is a white substance, only slightly soluble in water; used in ceramics and as an insecticide.

**Sodium Hydride** (NaH) — Prepared in white needle-like form by interaction between sodium vapour and hydrogen at  $400^\circ$  to  $450^\circ \text{C}$ . It yields hydrogen gas (and sodium hydroxide) with water.

**Sodium Iodide** — See Sodium Bromide.

**Sodium Manganate and Permanganate** — See Manganese (Compounds).

**Sodium Nitrate** ( $\text{NaNO}_3$ ) (m.p.  $308^\circ \text{C.}$ ) is easily obtained in a state of purity by recrystallization from its crude source (Chile nitre). The brine from Matsap Pan, in the Hague district of South Africa, contains, it is stated,  $4\frac{1}{2}$  tons of nitrates (chiefly sodium nitrate) in every 20,000 gallons of brine. It is a somewhat deliquescent and very soluble salt, 100 parts water dissolving nearly 69 parts at  $0^\circ \text{C.}$  and 102 parts at  $40^\circ \text{C.}$  Apart from its use in connection with the production of nitric acid, and the curing of meat (to preserve the colour), it is of value in mining, manufacture of military detonating explosives, firework-making, as a fertilizing agent, a flux in the glass industry, and for use in the production of potassium nitrate. (See Caliche, and Potassium (Nitrate).)

**Sodium Nitrite** ( $\text{NaNO}_2$ ) is a stable crystalline salt, of m.p.  $271^\circ \text{C.}$ , resulting from reduction of the nitrate by heating with metallic lead above its fusion-point ( $450^\circ$  to  $500^\circ \text{C.}$ ). It is produced by the electric-arc process of nitrogen fixation from air by treatment of the resultant gas with sodium carbonate solution, and subsequent crystallization. It is used in the dye industry, making nitric oxide, the economical curing of pork, tongues, and beef, and as a substitute for potassium nitrite.

**Sodium Phosphates** are commercially prepared by the action of phosphoric acid upon sodium carbonate or caustic soda. The chief one is the common or disodium hydrogen orthophosphate. It is an efflorescent, crystalline salt of composition  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ , which becomes anhydrous upon heating, and is used in various trades, including the compounding of baking-powder. Other crystalline phosphates are the normal sodium orthophosphate (trisodium phosphate) ( $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ ), used in medicine, and as described below; and sodium dihydrogen phosphate ( $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ), which is also used in making baking-powders. All these phosphates are soluble in water.

Trisodium phosphate is manufactured by churning a boiling solution of soda-ash (which can be prepared from "Trona") with a calculated amount of strong phosphoric acid, and subsequently treating the solution of the  $\text{Na}_2\text{HPO}_4$  thus produced with a strong solution of caustic soda, the several reactions being represented as:  $\text{Na}_2\text{CO}_3 + \text{H}_3\text{PO}_4 = \text{Na}_2\text{HPO}_4 + \text{CO}_2 + \text{H}_2\text{O}$ , and  $\text{Na}_2\text{HPO}_4 + \text{NaOH} = \text{Na}_3\text{PO}_4 + \text{H}_2\text{O}$ , the tribasic salt being crystallized out from the final product as  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ , which loses 11  $\text{H}_2\text{O}$  at  $100^\circ \text{C.}$  It is effective for the treatment of high-pressure boiler-feed water up to pressures of 1,000 pounds per square inch when used together with a small proportion of caustic soda, resulting in the deposition of calcium as phosphate and magnesium as phosphate or hydroxide. A 15 per cent. solution at  $70^\circ \text{C.}$  is useful as a detergent for cleaning glassware and otherwise as a general emulsifying and cleansing agent.

The so-called *microcosmic salt* ( $\text{NaH}(\text{NH}_4)\text{PO}_4 \cdot 4\text{H}_2\text{O}$ ) is a crystalline salt corresponding to  $\text{NaH}_2\text{PO}_4$ , in which an atom of hydrogen is

replaced by ammonium ; obtained by mixing solutions of ordinary sodium phosphate and ammonium chloride.

**Sodium Hexametaphosphate**  $((\text{NaPO}_3)_6$  or  $\text{Na}_6\text{P}_6\text{O}_{18})$  is used to soften water, since it has the property of reacting with calcium, magnesium, and other heavy-metal ions to include them in a complex ion and thus preventing their precipitation. (See G. O. Hall and C. Schwartz on "Sanitary Value of Sodium Metaphosphate in Dish-washing (*Ind. Eng. Chem.*, 29, 421 (1937)).)

**Sodium Pyrophosphate**  $(\text{Na}_4\text{P}_2\text{O}_7, 6\text{H}_2\text{O})$  is an opaque, crystalline white salt, derived from pyrophosphoric acid  $(\text{H}_2\text{P}_2\text{O}_7)$ .

**Sodium Phosphites** — Of these, there are two, which are represented by the formulæ  $\text{Na}_2\text{HPO}_3$  and  $\text{NaH}_2\text{PO}_3$  obtained from phosphorous acid  $(\text{H}_3\text{PO}_3)$ .

**Sodium Hypophosphite**  $(\text{NaH}_2\text{PO}_2, \text{H}_2\text{O})$  is used in medicine.

**Sodium Silicate (Soluble Glass, or Water-Glass)** is made by calcining either pure diatomaceous earth, quartz, or finely powdered flint or sand with caustic soda or sodium carbonate and (sometimes) powdered coal or coke, followed by extraction with water. Prepared in this way it is probably an indefinite mixture, the fused "lump silicate" varying in composition, being alkaline or neutral according to the composition of the charge. Silicon dioxide fused with sodium carbonate gives the soluble silicate  $\text{Na}_4\text{SiO}_4$ .

The following mixtures have been recommended for making lump water-glass in reverberatory furnaces : (a) 100 kilograms sand, 60 kilograms  $\text{Na}_2\text{SO}_4$ , 30 kilograms soda carbonate, 3 kilograms coke ; (b) 150 kilograms sand, 80 kilograms  $\text{Na}_2\text{SO}_4$ , 20 kilograms soda carbonate, 3 kilograms coke ; (c) 100 kilograms sand, 68 kilograms  $\text{Na}_2\text{SO}_4$ , 32 kilograms soda carbonate, 3 kilograms coke ; (d) 100 kilograms sand, 50 kilograms  $\text{Na}_2\text{SO}_4$ , 16 kilograms soda carbonate, 3 kilograms coke. Water-glasses that result are practically neutral, soluble in water with a very slight residue, giving easily filterable solutions, bluish-green to white in colour, which can be decolourized with charcoal if required.

Sodium silicate is known both in the anhydrous form  $(\text{Na}_2\text{SiO}_3)$ , and as  $\text{Na}_2\text{SiO}_3, 9\text{H}_2\text{O}$  ; is soluble in water (the limits for complete solubility being about 21.5 to 42.1 per cent.  $\text{SiO}_2$  and 5.25 to 26.95 per cent.  $\text{Na}_2\text{O}$ ), and is used in dyeing, calico-printing, grease-proofing paper, for the reclamation of crankcase oils, the facing or lining of corrugated paper, hardening concrete, iron enamelling, in the built-up paper-board industry, fire-proofing fabrics, making adhesives, paints, distempers, artificial stone, cements, soaps, etc., and as a cleansing and preservative agent.

It is marketed both as glass and in liquid form of 140° Tw. Some 85 per cent. of the world output of silicate is stated to be used in the soap and corrugated box industries. When employed in abrasive wheels the addition of about 4 per cent. of potassium permanganate is recommended.

In solution (as so-called water-glass) it is largely used as a cleansing agent and for preserving eggs, the shells being made air-tight by dip-

ping therein and drying, thus preventing the access of air-borne germs. It is also used for the preservation of stone-facings. It has similarly been recommended, as a binding agent, for the surface treatment of concrete roads and hardening concrete constructions owing to its formation of calcium silicate with the hydrated lime set free following the setting of cement, thus producing a non-porous hard coating and reducing the cost of upkeep. S. Mantel states that the silication of limestone depends upon the separation of silica in the pores of the limestone as a result of hydrolytic action. It can be used for making dustless concrete floors. The metasilicate ( $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ) is used as a laundry detergent. The sesquisilicate ( $3\text{Na}_2\text{O} \cdot 2\text{SiO}_2 \cdot 11\text{H}_2\text{O}$ ) is more alkaline (has a higher  $p\text{H}$ ) in solution than the metasilicate, and less alkaline (has a lower  $p\text{H}$ ) than sodium hydroxide. (See "The Role of Silica-Soluble Cleansers," by J. G. Vail (*Ind. Eng. Chem.*, **28**, 294 (1936)) ; J. G. Vail on *Soluble Silicates in Industry* (Reinhold Publishing Corp., New York) ; Adhesives, and Concrete.)

**Sodium Stannate** — See Tin (Compounds).

**Sodium Stannite** — See Tin (Compounds).

**Sodium Tungstate** — See Tungsten.

**Sodium Vanadate** ( $\text{Na}_3\text{VO}_4 \cdot 16\text{H}_2\text{O}$ ) is a white crystalline salt soluble in water, used in making aniline black and ink.

The sodium-organic compounds are arranged here alphabetically.

**Sodium Acetate** ( $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ ) is a colourless, crystalline, efflorescent body soluble in water, and has commercial applications, including preservation of meat and preparation of mordants.

**Sodium Aurothiomalate** ("Myocrisin") — A pale yellow salt, prepared by interaction of gold iodide solution and sodium thiomalate, very soluble in water. It is used in medicine for the treatment of arthritis and other forms of rheumatism.

**Sodium Benzoate** ( $\text{NaC}_7\text{H}_5\text{O}_2$ ) is a crystalline salt soluble in water ; used as a food preservative, and in medicine.

**Sodium Carboxymethyl Cellulose (Sodium CMC)** (Du Pont) — Used in the textile, paper, and cosmetic industries as a protective film, a sizing agent, and an emulsifier.

**Sodium Citrate** ( $2\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 11\text{H}_2\text{O}$ ) — A white, soluble crystalline salt ; used in medicine and for compounding non-alcoholic drinks.

**Sodium Cyanide** is produced quantitatively by the passage of carbon monoxide and ammonia gas over finely divided soda at from  $600^\circ$  to  $650^\circ$  C. It is also made by passing ammonia through melted sodium mixed with charcoal. It is a very poisonous compound and chiefly used for the extraction of gold and silver from ores. "Cyanegg" (Du Pont) is the trade-mark for 96 per cent. strength sodium cyanide in pellet form ; "Cyanoflake" in flakes ; and "Cyanogran" in granules. (See Cyanogen.)

**Sodium Ethoxide** ( $\text{C}_2\text{H}_5\text{ONa}$ ) — Produced by the action of metallic sodium on absolute alcohol and used as a synthetic agent.

**Sodium Ferricyanide and Ferrocyanide (Prussiates)** are soluble salts resembling the corresponding potassium salts, and are used industrially for the same applications, the ferrocyanide being also used in the

smelting of ashes and residues of non-ferrous metals. (See Potassium (Ferricyanide and Ferrocyanide).)

**Sodium Formate** ( $\text{NaCHO}_2$ ) — A soluble salt which can be prepared in a crystalline anhydrous state and also in association with water ( $\text{NaCHO}_2 \cdot \text{H}_2\text{O}$ ); used in making formic and oxalic acids, and carbon monoxide in the laboratory.

**Sodium Glycerophosphate** ( $\text{Na}_2\text{C}_3\text{H}_7\text{PO}_6 \cdot \text{H}_2\text{O}$ ;  $\text{C}_3\text{H}_5(\text{OH})_2\text{OPO}(\text{ONa})_2$ ) — A yellow viscid liquid, soluble in water and alcohol; used in medicine. It is also known in crystalline form as prepared by heating glycerol with monosodium phosphate and splitting off a molecule of glycerol from the diglycerol phosphate by means of caustic soda.

**Sodium Glutamate** (Sodium Salt of Alpha-Amino Glutaric Acid)  $\left( \begin{array}{cc} \text{COONa} & \text{COONa} \\ | & | \\ \text{CH}_2 - \text{CH}_2 - & \text{CH}(\text{NH}_2) \end{array} \right)$  — Used as a condiment.

**Sodium Lauryl Sulphate** — A white or slightly off-white powder, being a mixture of the sodium salts of normal primary alkyl sulphates, chiefly sodium lauryl sulphate. It is used in medicine as an emulsifying agent in the formulation of emulsified ointment bases and for the preparation of cosmetic creams. A commercial grade, under the name of "Dreft," is marketed as a scouring agent. (See Waxes (Emulsifying Wax).)

**Sodium Malate** ( $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6$ ) is a white, crystalline salt, and sometimes used in place of sodium chloride in food (see "Ekasalt").

**Sodium Naphthionate** ( $\text{C}_{10}\text{H}_6(\text{NH}_2)\text{SO}_2\text{ONa} \cdot 4\text{H}_2\text{O}$ ), a colourless crystalline intermediate soluble in water.

**Sodium Nitroprusside** ( $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$ ), a red crystalline salt soluble in water, used as a reagent in testing for soluble sulphides, and for some technical purposes.

**Sodium Oxalates** — The white normal salt ( $\text{Na}_2\text{C}_2\text{O}_4$ ) and the acid salt ( $\text{NaHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ) are both crystalline and soluble in water, and are used in the leather, tanning, and textile industries. The normal salt occurs in *varech*, also in a number of other plants. (See Oxalic Acid.)

**Sodium Phenate** (or **Carbolate**) ( $\text{C}_6\text{H}_5\text{ONa}$ ) is a white, deliquescent, crystalline salt, prepared from phenol and caustic soda by mixing and heating in an autoclave (by which means the compound is desiccated); it is soluble in water and alcohol; and used in the manufacture of salicylic acid and as an antiseptic, etc.

**Sodium Salicylate** ( $\text{NaC}_7\text{H}_5\text{O}_3$ ), a white crystalline salt soluble in water and used in medicine; prepared from sodium phenoxide and carbon dioxide by heating in an autoclave.

**Sodium Tannate** — A compound of tannic acid (gallotannic acid) and soda; used in dyeing and for removing incrustations in boilers.

**Sodium Tartrate** ( $\text{Na}_2\text{C}_4\text{H}_4\text{O}_6 \cdot 2\text{H}_2\text{O}$ ) is a white crystalline salt soluble in water; used in medicine.

**Sodium Thiocyanate** (Sulphocyanide) ( $\text{NaCNS}$ ) — Made by heating sulphur in sodium cyanide solution; used in bismuth refining.

**"SOFNOL"** — A specially prepared calcium hydroxide for the softening of waters. Other "Sofnol" mixtures for different qualities of water are the "Sofnol lime-soda mixture" and the caustic soda and soda-ash mixture known as the "Sofnol marine mixture." As to the last named, the caustic soda is used to remove the magnesium salts and the carbon dioxide. "Sofnol soda-lime G" is an activated grade containing a fractional quantity of manganic acid, and is reported to have a much greater absorptive capacity than ordinary soda-lime for carbon dioxide. "Sofnolite" is a modified soda-lime prepared for analytical purposes. (See Filters, and Water Softening.)

**SOILS** — The outer crust of the earth covering the geological foundations of the land, consisting mainly of various mineral matters resulting from weathering, through the action of air, water, and other agencies upon rocks, and mixed with organic (humous) substances derived from the decay of vegetable growths and animal matter. It has been conjectured that beneath the earth's surface for the depth of some 18 miles there is a mass of rocky siliceous compounds named *sial*, and, beneath that again, a material of greater density named *sinia*, while the central core (the composition of which is a matter of much speculation) consists of an alloy of iron and nickel at a depth of some 2,450 kilometres (see Earth). Beneath the sea, however, there is no *sial*, but the *sinia* starts immediately.

The chemical constitution of soils (from which plants obtain their mineral food) varies according to the nature of the rocks from which they have resulted and the processes which have taken place and are in course of action (soil genetics), and they are roughly described as of sand, chalk, clay, or loam, etc., according to the prevailing features. It has been suggested that the soil possesses some of the attributes of colloids, with respect to its powers of absorption and retention of water, and the soil moisture is certainly of great importance, inasmuch as it constitutes the nutrient solution for growing vegetation.

The plant residual products present in soil furnish the micro-organisms in it with food, the two more important ones being cellulose and proteins, which give rise respectively to humus and ammonia. The humus exercises important physical effects in the soil, and it is from the ammonia, which becomes bacterially oxidized to form nitrates, that growing crops obtain their nitrogenous food, the two groups of organisms which effect this fixation being the *Azotobacter* and *B. amylobacter*. A sporing organism which easily decomposes cellulose in contact with the air is named *Spirochaeta cytophaga*, and gives a simple nitrogen compound such as a nitrate or ammonia; it produces, among other things, a pigment like carotin. During the growth of clover, lucerne, in vetches, peas, beans, etc., fixation of nitrogen proceeds vigorously. Certain bacteria and fungi bring about the decomposition of protein, and active bacterial activity occurs, it is stated, to a depth of from 20 to 25 inches below the soil surface. Two soil organisms which flourish particularly in soil dressed with farmyard manure are *fluorescens* and *Ps. caudatus*.

In addition to bacteria many other micro-organisms are found in

soils. These include protozoa of various kinds, fungi, and others. These may assist in the process of organic matter decomposition, or in some cases they may compete with the normal bacterial flora and thus result in unhealthy soil conditions. Occasionally it becomes necessary to treat the soil with heat or with fumigants such as chloropicrin, formaldehyde, or chlorinated hydrocarbons to reduce the population of undesirable and pathogenic organisms present.

Soil colours have been classified, using Ostwald's colour disc, by Archangelskaya (1932).

Of the twenty or more chemical **elements** that are present in all soils the following are **essential** to plant growth, namely, nitrogen, phosphorus, potassium, calcium, magnesium, iron, and sulphur. In general, all but three of these elements, namely, nitrogen, phosphorus, and potassium are present in sufficient amounts for the requirements of all farm crops. These three are critical elements of soil productivity, and constitute the chief desired ingredients of fertilizers that are added to enrich soils.

The **acidity** of soils is due to free aluminosilicic acid and humic acid, which, in the presence of air, by combination with the fertilizer base, yield free acidity, while "exchange" acidity is produced when soil is treated with a neutral salt, such as a potassium or nitrogenous fertilizer, through the exchange of a base of soil silicates with that of the fertilizer used. If these silicates contain much iron or aluminium, salts are produced which are acid and toxic to plants. The "reaction" of soil is easily and quickly tested. Acid soils are infertile to most crops except potatoes, but the acidity can be remedied by liming, which renders potassium and phosphoric fertilizers more available, accelerates the conversion of nitrogenous fertilizers into ammonia, and favours the action of nitrifying bacteria, which develop more abundantly in a slightly alkaline soil. Liming is carried out by the use of lime, or marl, etc. (See pH Value.)

*References:* *Soil Conditions and Plant Growth*, by E. J. Russell (Longmans, Green and Co., London); *The Physical Properties of the Soil*, by B. A. Keen (Longmans, Green and Co., London); the Rothamsted Reports of the Lawes Agricultural Trust at Harpenden; *Principles of Plant Biochemistry*, by M. W. Onslow (Part I) (Cambridge Univ. Press); *Transactions of the Third International Congress of Soil Science*, Oxford, 1935, Vols. 1-3 (Thomas Murby and Co., London) (First Congress, Washington, 1927; Second Congress, Leningrad and Moscow, 1930); *Soils: Their Origin, Constitution and Classification*, by G. W. Robinson (T. Murby and Co., London); *Nature and Properties of Soils*, by Lyon and Buckman (Macmillan, London and New York); *Principles of Soil Technology*, by Emerson (Macmillan, London and New York); *Soils: Their Physics and Chemistry*, by A. N. Puri (Reinhold Publishing Corp., New York); *Soilless Growth of Plants*, by Carleton Ellis and M. W. Swaney (Reinhold Publishing Corp., New York); *Bacteria, Fertilizers, and Humus*.

**SOLANIN** (*Solanum* species) ( $C_{32}H_{61}O_{11}N$ ) — A poisonous glycoside constituent of potatoes contained to the extent of from 0.02 to 0.1 part per thousand, and present in the young shoots up to 50 parts per thousand; m.p.  $214^{\circ}C.$ ; soluble in 85 per cent. alcohol: also contained in bittersweet (*Solanum dulcamara*). The percentage contained in potatoes varies: in one reported case the amount was 0.0495 per cent., of which 0.0177 was in the peel, and in another case 0.079 per cent. was found, of which 0.0235 occurred in the peel. Three normal varieties of different kinds were found to contain respectively 2.0, 2.1, and 7.5 milligrams of solanine in 100 grams of potatoes, and in extreme cases quantities varying from 26 to upward of 58 milligrams per 100 grams of potatoes have been found. Solanine yields, upon hydrolysis, solanidine and a sugar.

**SOLDERS** — See Alloys.

**SOLIDS** — See Matter.

**" SOLIGENATES "** — Certain driers understood to be compounded of lead, manganese, and cobalt salts of naphthenic acids derived from the oxidation of petroleum; soluble in vegetable oils, turpentine, benzol, etc.

**" SOLOZONE "** — See Sodium Oxides.

**SOLS** — See Colloids.

**SOLUBILITIES** — See *Solubilities of Inorganic and Organic Substances*, by A. Seidell (D. Van Nostrand Co., New York); and Solution.

#### SOLID PHASE AND SOLUBILITY OF SELECTED IMPORTANT CHLORIDES, NITRATES, AND SULPHATES

Authority: *Solubilities of Inorganic and Organic Compounds*, A. Seidell (D. Van Nostrand Co., New York)

Data selected and arranged by the Editor.

Salt	Solid Phase	Solubility		Per	At ° C.
		Grams	Of		
<b>Aluminium</b>					
Chloride .. ..	$AlCl_3 \cdot 6H_2O$	41	$AlCl_3$	100 g. solution (Sp. gr. 1.354)	15
Sulphate .. ..	$Al_2(SO_4)_3 \cdot 18H_2O$	27	$Al_2(SO_4)_3$	100 g. solution	20
<b>Ammonium</b>					
Chloride .. ..	$NH_4Cl$	27	$NH_4Cl$	100 g. solution	20
Nitrate .. ..	$NH_4NO_3$	66	$NH_4NO_3$	100 g. solution	20
		72	$NH_4NO_3$	100 g. solution ( $32^{\circ}C.$ tr. pt.)	32
Sulphate .. ..	$(NH_4)_2SO_4$	43	$(NH_4)_2SO_4$	100 g. solution (Sp. gr. 1.241)	20
Hydrogen sulphate	$NH_4HSO_4$	77	$NH_4HSO_4$	100 g. solution	30
<b>Barium</b>					
Chloride .. ..	$BaCl_2 \cdot 2H_2O$	26	$BaCl_2$	100 g. solution	20
Nitrate .. ..	$Ba(NO_3)_2$	8	$Ba(NO_3)_2$	100 g. solution	20
Sulphate .. ..	$BaSO_4$	0.0024	$BaSO_4$	Litre solution	20
<b>Calcium</b>					
Chloride .. ..	$CaCl_2 \cdot 6H_2O$	43	$CaCl_2$	100 g. solution	20
Nitrate .. ..	$Ca(NO_3)_2 \cdot 4H_2O$	56	$Ca(NO_3)_2$	100 g. solution	20
Sulphate .. ..	$CaSO_4 \cdot 2H_2O$	0.20	$CaSO_4$	100 cc. solution	18

Salt	Solid Phase	Solubility		Per	At ° C.
		Grams	Of		
<i>Copper (cupric)</i>					
Chloride .. ..	$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	43	$\text{CuCl}_2$	100 g. solution (Sp. gr. 1.579)	17
Nitrate .. ..	$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	54	$\text{Cu}(\text{NO}_3)_2$	100 g. solution (Sp. gr. 1.681)	18
Sulphate .. ..	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	16	$\text{CuSO}_4$	100 g. solution (Sp. gr. 1.193)	16
<i>Iron (ferric)</i>					
Chloride .. ..	$\text{FeCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$	73	$\text{FeCl}_3$	100 g. solution	27
<i>Iron (ferrous)</i>					
Chloride .. ..	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	40	$\text{FeCl}_2$	100 g. solution	23
Nitrate .. ..	$\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	45	$\text{Fe}(\text{NO}_3)_2$	100 g. solution	18
Sulphate .. ..	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	26.5	$\text{FeSO}_4$	100 g. $\text{H}_2\text{O}$	20
<i>Lead (plumbous)</i>					
Chloride .. ..	$\text{PbCl}_2$	1.08	$\text{PbCl}_2$	100 cc. solution	25
		3.04	$\text{PbCl}_2$	100 cc. solution	95
Nitrate .. ..	$\text{Pb}(\text{NO}_3)_2$	34	$\text{Pb}(\text{NO}_3)_2$	100 g. solution (Sp. gr. 1.405)	17
Sulphate .. ..	$\text{PbSO}_4$	0.04	$\text{PbSO}_4$	Litre solution	20
<i>Magnesium</i>					
Chloride .. ..	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	35	$\text{MgCl}_2$	100 g. solution	20
Nitrate .. ..	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	42	$\text{Mg}(\text{NO}_3)_2$	100 g. solution (Sp. gr. 1.384)	18
Sulphate .. ..	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	26	$\text{MgSO}_4$	100 g. solution	20
<i>Manganese (Manganous)</i>					
Chloride .. ..	$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	43	$\text{MnCl}_2$	100 g. solution	20
Nitrate .. ..	$\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	57	$\text{Mn}(\text{NO}_3)_2$	100 g. solution	18
Sulphate .. ..	$\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$	39	$\text{MnSO}_4$	100 g. solution	23
<i>Nickel (ous)</i>					
Chloride .. ..	$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	39	$\text{NiCl}_2$	100 g. solution	20
Nitrate .. ..	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	49	$\text{Ni}(\text{NO}_3)_2$	100 g. solution	20
Sulphate .. ..	$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$	27	$\text{NiSO}_4$	100 g. solution	22
<i>Potassium</i>					
Chloride .. ..	$\text{KCl}$	25	$\text{KCl}$	100 g. solution	20
Nitrate .. ..	$\text{KNO}_3$	24	$\text{KNO}_3$	100 g. solution	20
		67	$\text{KNO}_3$	100 g. solution	90
Sulphate .. ..	$\text{K}_2\text{SO}_4$	10	$\text{K}_2\text{SO}_4$	100 g. solution	20
Hydrogen sulphate ..	$\text{KHSO}_4$	51	$\text{KHSO}_4$	100 g. $\text{H}_2\text{O}$	20
<i>Silver</i>					
Chloride .. ..	$\text{AgCl}$	0.0016	$\text{AgCl}$	Litre solution	20
Nitrate .. ..	$\text{AgNO}_3$	68	$\text{AgNO}_3$	100 g. solution	20
Sulphate .. ..	$\text{Ag}_2\text{SO}_4$	0.8	$\text{Ag}_2\text{SO}_4$	100 g. solution	20
<i>Sodium</i>					
Chloride .. ..	$\text{NaCl}$	26	$\text{NaCl}$	100 g. solution	20
		28	$\text{NaCl}$	100 g. solution	90
Nitrate .. ..	$\text{NaNO}_3$	47	$\text{NaNO}_3$	100 g. solution	20
		62	$\text{NaNO}_3$	100 g. solution	90
Sulphate .. ..	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$	16.3	$\text{Na}_2\text{SO}_4$	100 g. solution (Sp. gr. 1.155)	20
	$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ — $\text{Na}_2\text{SO}_4$	33.6	$\text{Na}_2\text{SO}_4$	100 g. solution (Sp. gr. 1.323) (32.4° C. tr. pt.)	32.4
Hydrogen sulphate	$\text{NaHSO}_4$	29	$\text{NaHSO}_4$	100 g. $\text{H}_2\text{O}$	25
<i>Zinc</i>					
Chloride .. ..	$\text{ZnCl}_2 \cdot \text{H}_2\text{O}$	80	$\text{ZnCl}_2$	100 g. solution	20
	$\text{ZnCl}_2 \cdot \text{H}_2\text{O}$ — $\text{ZnCl}_2$	81	$\text{ZnCl}_2$	100 g. solution (28° C. tr. pt.)	28
Nitrate .. ..	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	54	$\text{Zn}(\text{NO}_3)_2$	100 g. solution	18
Sulphate .. ..	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	34	$\text{ZnSO}_4$	100 g. solution (Sp. gr. 1.452)	15

## SOLID PHASE AND SOLUBILITY OF SELECTED IMPORTANT CARBONATES AND HYDROXIDES

Authority: *Solubilities of Inorganic and Organic Compounds*, A. Seidell  
(D. Van Nostrand Co., New York)

Data selected and arranged by the Editor.

Compound	Solid Phase	Solubility		Per	At ° C.
		Grams	Of		
<b>Ammonium</b>					
Hydrogen carbonate	$\text{NH}_4\text{HCO}_3$	17	$\text{NH}_4\text{HCO}_3$	100 g. solution	20
<b>Barium</b>					
Carbonate .. ..	$\text{BaCO}_3$	0.02	$\text{BaCO}_3$	Litre water	18
Hydroxide .. ..	$\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$	4	$\text{Ba}(\text{OH})_2$	100 g. solution	20
		50	$\text{Ba}(\text{OH})_2$	100 g. solution	80
<b>Calcium</b>					
Carbonate .. ..	$\text{CaCO}_3$	0.07	$\text{CaCO}_3$	Litre water	20
Hydroxide .. ..	$\text{Ca}(\text{OH})_2$	0.2	$\text{Ca}(\text{OH})_2$	100 g. water	20
<b>Magnesium</b>					
Carbonate .. ..	$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$	2.4 (?)	$\text{MgCO}_3$	Litre solution	18
Hydroxide .. ..	$\text{Mg}(\text{OH})_2$	0.008	$\text{Mg}(\text{OH})_2$	Litre solution	18
<b>Potassium</b>					
Carbonate .. ..	$\text{K}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$	53	$\text{K}_2\text{CO}_3$	100 g. solution	20
Hydrogen carbonate	$\text{KHCO}_3$	25	$\text{KHCO}_3$	100 g. solution	20
Hydroxide .. ..	$\text{KOH} \cdot 2\text{H}_2\text{O}$	53	$\text{KOH}$	100 g. solution	20
<b>Sodium</b>					
Carbonate .. ..	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	22	$\text{Na}_2\text{CO}_3$	100 g. water	20
	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ — $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	45	$\text{Na}_2\text{CO}_3$	100 g. water (33.1° C. tr. pt.)	33.1
Hydrogen carbonate	$\text{NaHCO}_3$	9	$\text{NaHCO}_3$	100 g. solution	20
Hydroxide .. ..	$\text{NaOH} \cdot \text{H}_2\text{O}$	52	$\text{NaOH}$	100 g. solution	20

## SOLUBILITY OF GASES IN WATER

Gas	Solubility Standard c.c. of Gas at 760 mm. Hg per 100 c.c. of Water.
<b>Very soluble :</b>	
Ammonia .. ..	58,600 at 25° C.
Hydrogen chloride .. ..	50,300 at 0° C.
Sulphur dioxide .. ..	1,550 at 60° C.
<b>Medium soluble :</b>	
Acetylene .. ..	110 at 20° C.
Carbon dioxide .. ..	90 at 20° C.
Hydrogen sulphide .. ..	260 at 20° C.
Nitrous oxide .. ..	60 at 25° C.
<b>Slightly soluble :</b>	
Carbon monoxide .. ..	2.3 at 20° C.
Hydrogen .. ..	1.8 at 20° C.
Methane .. ..	6 at 20° C.
Nitric oxide .. ..	5 at 20° C.
Nitrogen .. ..	1.5 at 20° C.
Oxygen .. ..	3.1 at 20° C.

**SOLUTE** — See Solution.

**SOLUTION AND SOLVENT ACTION** — Salt placed in water gradually disappears. The salt is *dissolved* and constitutes the *solute*, whilst the *solvent* (water), which was previously tasteless, becomes saline in taste, and constitutes a *solution* of salt or a homogeneous mixture presenting a single phase. (See Colloid Chemistry.) Many other liquids have this power of dissolving solid substances, the products being homogeneous mixtures. There are cases known in which there are increased solubilities of substances in mixed solvents when the solute is only slightly soluble in only one of the solvents. Again, many liquids have the power of absorbing or dissolving certain gases; ammonia, hydrogen chloride, sulphur dioxide, and chlorine are all soluble in water, absorption in this sense being the same thing as solution or solubility. Further, many liquids, such as certain oils and hydrocarbons, are soluble in alcohol, ether, and some other liquids, and solution in this sense is identical with that of a solid substance dissolved in a liquid.

Gases also have the property of holding substances in solution; air, for example, will take up a given quantity of water according to the temperature, and the mixture may be regarded as one of water dissolved in air. (See Air, Dew Point, and Hygrometers.)

Solutions of solids in solids are also known, solid solutions being defined as solid homogeneous complexes of several substances, presenting a single phase. Isomorphic mixtures are solid solutions. The proportions of the several substances may vary without affecting the homogeneity. Solid solutions may also result from occlusion of gases in charcoal and occur in mixed crystals.

When a substance is dissolved in water there is generally a fall in temperature, and the amount of heat which disappears (or is evolved) when a definite amount of the substance is dissolved in a solvent is known as the **heat of solution**; that for 1 gram-molecule of sodium chloride (58.5 grams) in 100 gram-molecules of water (1,800 grams) being -1,280 calories. The lowering of the temperature upon dissolving most salts is believed to be connected with the fact that the solubility of most salts is greater the higher the temperature at which solution occurs. Salts of opposite solubility characteristics raise the temperature of water upon dissolving in it. (See Refrigeration.)

There are certain conditions under which some solutions solidify as a whole. Solidified mixtures of solute and solvent (water), which are of the same composition as the solution are known as **eutectics**. (See Solubilities).

As a general rule, the solubility of a solid in a liquid increases with the temperature, and when a solution will not dissolve any more of the substance at any particular temperature it is said to be *saturated*. A solution is said to be *dilute* in character when it contains but little of its particular ingredient, and is described as strong or *concentrated* when the proportion of dissolved substance is great in quantity. Many solutions which are not already saturated can be strengthened or concen-

trated by evaporation of some of the solvent. For instance, a dilute solution of sodium nitrate in water may be concentrated by the application of heat (which causes the evaporation of some of the water), or upon allowing to remain in the open air, to such a stage that, when cooled, or with the lapse of sufficient time in the second case, the excess of the salt crystallizes out. On the other hand, strong solutions can be weakened (*diluted*) by the addition of more solvent. *Super-saturated* solutions are those that contain *in solution* more of the given substance than corresponds to a saturated solution. These are usually obtained by cooling a solution, saturated at a higher temperature, to a lower temperature in the absence of crystal nuclei. (See Sir Henry Miers in *J.C.S.*, **89**, 413 (1906) ; Crystals, and Solvents.)

With respect to electrolytic dissociation of electrolytes in solution into ions, the amount split up is the greater, the greater the dilution, in the case of weak electrolytes (Ostwald's Dilution Law). (See Electricity, and Electrolytic Dissociation.)

"Normal" and "standardized" solutions are described under the heading of Volumetric Analyses.

**SOLVENT EXTRACTION** -- See Extraction.

**SOLVENT NAPHTHA** — See Benzol, Coal, Naphtha, and Petroleum.

**SOLVENTS** — In addition to water (the greatest general solvent), acetone, ethyl alcohol, normal and isopropyl alcohols, tertiary butyl alcohol, ethylene glycol, cyclohexanol, methylcyclohexanol, diacetone alcohol, many esters, benzene, petrol, naphtha, carbon tetrachloride, carbon disulphide, turpentine, and other agents, and a number of colourless chlorinated organic solutions have in recent years come into extensive use in connection with fats, oils, paints, rubber, etc. Some of these solvents are displayed under Acetylene (Chart II), and Ethylene (Chart).

Dichloroethylene and trichloroethylene are particularly favoured on account of their non-inflammable character, their chemical stability and resistance to hydrolysis, while their vapours do not form explosive mixtures with air, and do not attack the metallic parts of chemical plants. Trichloroethylene is relatively harmless, but the vapour of tetrachlorethane is highly poisonous. Ethylene dichloride (see same) can be used without danger, presents a very low fire hazard, and its chemical stability and resistance to hydrolysis give it advantages as a solvent over carbon tetrachloride.

Several amylene dichlorides (dichloropentanes) are used as solvents of wax, tar, oils, gums, resins, rubber, etc. Solvents are variously used for the purposes above mentioned, as also for dry cleaning garments and in the rubber, varnish, paint, lacquer, and solvent soap industries.

Dichlorodiethyl ether ( $(\text{CICH}_2\text{CH}_2)_2\text{O}$ ) is a solvent that boils at  $178^\circ\text{C}$ ., is insoluble in water but soluble in alcohol, ether, and benzene, and can be used for dissolving fats and "spotting" cellulose acetate fabrics ; also as a general cleansing agent.

Another solvent is a derivative of ethylene named "Dioxane," (diethylenedioxiide)  $\left( \text{O} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{O} \right)$  a colourless liquid of faint, pleasant odour, miscible with water and the usual organic solvents; m.p.  $12^\circ \text{C.}$ ; b.p.  $101.5^\circ \text{C.}$ ; sp. gr. 1.035; and ref. ind. 1.4238 at  $18^\circ \text{C.}$  It is described as an excellent solvent for resins of the alcohol and oil soluble types, vegetable and mineral oils, greases, blown linseed and other oils, certain waxes (including beeswax and carnauba wax), and it can be employed in the manufacture of various types of lacquers, celluloid, varnishes, polishes, paints, etc., and other products dependent upon the employment of nitrocellulose, cellulose acetate, etc. The use of "Dioxane" is not without health hazards.

The consumption of solvents was estimated by H. C. Holden and A. K. Doolittle (*Ind. Eng. Chem.*, **27**, 525 (1935)) to be distributed as follows: industrial alcohol and turpentine 58 per cent. by volume, pyroxylin lacquer solvents and coal tar distillates 15 per cent., glycerol, glycol, and methyl alcohol 12 per cent., carbon disulphide and acetone 10 per cent., and all others (exclusive of petroleum distillates) 5 per cent.; and of the total solvents consumed some 15 per cent. are utilized in the plastics, adhesives, and artificial fibre industries, the principal solvents thus used being carbon disulphide, acetone, methyl and ethyl alcohols.

(See "The Handling of Organic Solvents" (Industrial Safety), by R. Brightman (*Ind. Chem.*, **6**, 209 (1930)); "The Solvent Extraction of Vegetable Oils, by A. E. Williams (*Ind. Chem.*, **7**, 161 (1931)); "Solvent Recovery by the Bayer Active Carbon Process in the Manufacture of Cordite," by J. C. Liddle (*Chem. and Ind.*, **51**, 3 (1932)); J. B. Hill on solvent extraction processes in the petroleum industry in *Ind. Eng. Chem.*, **27**, 522 (1935); "Solvents and Plasticizers, 1918-1938," by Carleton Ellis (*Chemical Industries*, New York, **43**, 145 (1938)); *Solvents*, by T. H. Durrans (Chapman and Hall, London); *Volatile Solvents and Thinners*, by Noël Heaton (E. Benn, London); *Organic Solvents*, by A. Weissberger and E. Proskauer (Clarendon Press, Oxford); *Toxicity of Industrial Organic Solvents* (H.M. Stationery Office, London); *Technology of Solvents*, by O. Jordan (Reinhold Publishing Corp., New York); *Industrial Solvents*, by Ibert Mellan (Reinhold Publishing Corp., New York); Aluminium (Activated Alumina), Carbon (Activated), and Silica (Silica Gel).)

**SOMBRERITE** — An impure mineral calcium phosphate ( $\text{Ca}_3(\text{PO}_4)_2$ ) found in Sombrero and other islands of the Antilles.

**"SONERYL"** — See Butobarbitone.

**SOOT** finds use as an effective mild soil fumigant, particularly when used fresh, and has some value as a fertilizer for cereals and grass by reason of its ammonium sulphate content.

**SORBIC ACID** ( $\text{C}_6\text{H}_7\text{COOH}$ ) — Found in the unripe sorb apple (*Sorbus aucuparia*) and mountain-ash berries.

**SORBITOL** ( $C_6H_8(OH)_6$ ) — A hexahydric alcohol, m.p.  $110^\circ C.$ , obtainable as an 85 per cent. syrup by the reduction of dextrose. It is used in making resins, as a softening and moistening agent for textiles, papers, and leathers, and was formerly the starting material for synthetic vitamin C, before the synthesis employing the more easily obtained *l*-galactose was introduced.

**"SOREL CEMENT"** — A strong binding, made by mixing calcined magnesia with concentrated solution of magnesium chloride, which sets to a hard mass of the composition  $MgCl_2 \cdot 5MgO \cdot xH_2O$  (the value of  $x$  being about 17). It is extensively used in combination with various fillers, such as asbestos, cork-dust, wood flour and sawdust for interior finishing, such as stucco, flooring, and building materials. Its corrosive action on ironwork is stated to be obviated by the substitution of ferrous chloride in sufficient quantity for magnesium chloride in the making. This product is blue, but turns brown upon exposure to the air, and although possessing the advantage indicated, it is said to be not completely water-resistant.

Another cement, said to be impervious to water and oils, consists of a mixture of chlorides of zinc or magnesium and ammonium with oxide of magnesium or zinc, which interact, forming oxychlorides, to which hardening agents, such as powdered glass, sodium borate, silica, and flowers of zinc are added. The ammonium chloride retards the setting, so that the mixture may be readily applied by brush or trowel, and a small addition of zinc sulphate still further retards the setting. Contact with water increases the hardness when once set. (See "Xylolith".)

**SORGHUM** (*Durra-Sorgho*, *Sorghum Saccharatum*, *Kafir*, *Indian Millet*)

— A sugar-producing grass resembling maize in appearance, cultivated in the United States, and used for human food, cattle-feeding, and various industrial purposes, but not suitable for malting. Several species are cultivated in Asia and Africa, particularly the *S. vulgare*. The following percentage table is extracted from published analyses :

	Protein	Starch	Pentosans
Kafir kernels ( <i>S. caffrorum</i> ) . .	12.70	61.90	3.30
Milo " " " "	13.99	68.52	3.93
Feterita " " " "	16.69	64.16	3.38

According to C. K. McClelland, "Honey Sorghum" yields 15 to 238 (average 75) gallons of syrup per acre, and 30 to 45 per cent. of the cane weight is obtained as juice, the sugar content being 5.7 to 14.7 per cent.

Sorghum is largely used for the production of syrup.

The meal does not make good bread, but is stated to be an excellent substitute for rice in puddings.

**SORPTION** — See *Sorption of Gases by Solids*, by J. W. McBain (Routledge, London) ; Adsorption, and Colloid Chemistry.

**SORREL WOOD** — The wood of *Oxalis acetosella* (Fam. Oxalideæ), a plant indigenous to Britain and which contains potassium oxalate.

**SOXHLET APPARATUS** — A glass appliance used for the extraction of soluble parts of substances, such as fat from milk, by the action of volatile solvents.

**SOYA-BEAN (SOJA-BEAN, SOY-BEAN) OIL** — A Chinese and Japanese product expressed from soya beans (*Soja hispida* and *S. japonica*, N.O. Leguminosæ). It is used as an illuminant, also in margarine and soap-making, as a cattle food, oil in varnish-making, and in the preparation of so-called synthetic milk and cream. The cultivation of soya beans in the United States is rapidly expanding, the crop amounting to some 87,000,000 bushels in 1939, and is also carried on in India, Ceylon, South Africa, Australia, and South America; it is also reported that some successful attempts are being made to cultivate a variety of the beans in Britain. The percentage of oil in the beans varies from 14·6 to 25·6, and they are said to be rich in vitamins. After the removal of oil the remaining meal contains approximately 40 per cent. of protein, and various industrial uses for this have been proposed, including the production of plastics.

The oil has a pleasant odour and taste, is light brown in colour, and is generally credited with a sp. gr. of from 0·920 to 0·926; m.p. 28° C.; sap. v. 185 to 195; i.v. 128 to 135; ref. ind. 1·4673 at 40° C.; acid value 4; acet. value 17; and solidifying-point of -8° C.

One published analysis of the mammoth yellow variety gives a composition to the oil of 83·5 per cent. unsaturated acids, 11·5 per cent. saturated acids, and containing glycerides of linolenic acid 2·35 per cent., linolic acid 51·5 per cent., oleic acid 33·4 per cent., palmitic acid 6·8 per cent., stearic acid 4·4 per cent., arachidic acid 0·7 per cent., and lignoceric acid 0·1 per cent. Another analysis of this oil (by H. Peahler) is as follows: linolenic acid 1·9 per cent.; linoleic acid 29·2 per cent.; isolinoleic acid (including a little-isolinolenic acid) 24·3 per cent.; oleic acid 30·8 per cent.; stearic acid 7·0 per cent.; palmitic acid 2·35 per cent.; glyceryl residue (as  $C_3H_2$ ) 3·88 per cent.; and unsaponifiable matter 0·5 per cent. An analysis of the insoluble fatty acids of soya-bean oil (variety not named) is as follows: palmitic acid 10 per cent.; stearic acid 2 per cent.; arachidic acid 1 per cent.; lignoceric, linolenic, linolic, and oleic acids 88 per cent.

The cold-pressed oil is converted into a thick viscid product of sp. gr. 0·96 or over by heating it to 500° C. for from five to seven hours, and a liquid resembling petroleum is stated to result from heating a mixture of the oil and finely powdered Japanese acid clay at 700° C., also from the dry distillation of the calcium salts of the fatty acids of the oil.

The composition of the soya bean varies a good deal with the several varieties. Analyses of black and yellow soya beans from Bulgaria have shown them to contain 10·91 per cent. water, 36·76 per cent. protein, 18·57 per cent. fat, 25·27 per cent. nitrogen-free extract, 3·94 per cent. crude fibre, and 4·75 per cent. ash; while samples of

artificial milk made from the same beans gave on analysis 90.53 per cent. and 88.19 per cent. water, 5.3 and 6.04 per cent. protein, 2.21 and 2.94 per cent. fat, 1.18 and 1.90 per cent. carbohydrates, and 0.78 and 0.93 per cent. ash.

Both the beans and the oil are staple articles of food in China and Japan, also the residual cake after extraction of the oil, while in England the oil is chiefly used for soap-making, and, it is said, to some extent as a substitute for linseed, rape, and cotton-seed oils in respect of their various applications. The characteristics of nine varieties are given by G. S. Jamieson *et al.* in *Journal of Agricultural Research*, **46**, 57 (1933).

Soya-bean flour can be utilized in some measure for incorporation with ordinary flour in bread-making, and a good sauce (soy) of the "Worcester" type can be made from a mixture of soya beans and roasted wheat by subjecting it to mould fermentation, and then to prolonged maturing in brine.

Soya-bean cake is a valuable cattle food and a useful fertilizer.

(See Avent and Morgan on "Commercial Lecithin from Soya Beans" (*J.S.C.I.*, **51**, 169 T (1932)); "Composition of Soya-Bean Protein," by M. Mashino (*B.C.A.*, **A**, 1932, 182); "The Soybean," by W. L. Burlison (*Ind. Eng. Chem.*, **28**, 772 (1936)); "Soybean Oil in the Food Industry," by M. M. Durkee (*Ind. Eng. Chem.*, **28**, 898 (1936)); "Soybean Oil and the Paint Industry," by E. E. Ware (*Ind. Eng. Chem.*, **28**, 903 (1936)); *The Soya Bean and the New Soya Flour*, by C. J. Ferrée (W. Heinemann, London); *Soybeans and Soybean Products*, by K. S. Markley, editor (Interscience Publishers, New York).)

**SPACE FORMULAS** — See Formulas, and Stereochemistry.

**SPALLATION REACTION** — In nuclear bombardment the target nucleus emits a number of low-mass particles, but leaves behind a residual nucleus of relatively high mass, differing from the original target nucleus by up to 40 mass units less. The bombarding particles used are 200 Mev deuterons and 400 Mev alpha particles.

**SPALLING** — See Porosity, and Refractories.

**SPANISH FLIES** — See Cantharides.

**SPARTEINE SULPHATE** ( $C_{15}H_{26}N_2 \cdot H_2SO_4 \cdot 5H_2O$ ) — The sulphate of a dibasic, colourless liquid alkaloid obtained from the tops of *Cytisus scoparius* (Broom); soluble in water and alcohol; insoluble in ether; formerly used in medicine. The pharmacology of sparteine is described by Koppany in *J. Pharmacol.*, **72**, 23 (1941); Ligon in *J. Pharmacol.*, **73**, 151 (1941).

**SPATHIC IRON ORE** — See Iron, and Siderite.

**SPATULAS** — Flat blades used for transferring solid or pasty substances from one container to another; made of various materials, some of steel fixed in a wooden handle, others of porcelain, glass, ivory, platinum, nickel, aluminium, etc.; and used according to the nature of the substance to be manipulated.

**SPEARMINT OIL (Green Mint Oil)** — The volatile oil distilled from the fresh flowering herb of *Mentha viridis* in America or of *Mentha crispa* in Europe. It contains from 42 to 60 per cent. of carvone with terpineol, *l*-limonene, and *l*-pinene; soluble in alcohol and ether; sp. gr. 0.920 to 0.940 at 15° C.; opt. rot.  $-34^{\circ}$  to  $-55^{\circ}$  at 20° C.; ref. ind. 1.483 to 1.490 at 20° C. Used as a flavouring agent. (See Peppermint Oil.)

**SPECIFICATIONS** — See Standard Specifications.

**SPECIFIC GRAVITIES** — The relative weights of equal volumes of gases compared with hydrogen at 0° C. and 760 mm. as unit are known as their specific gravities or vapour densities. (See Vapour Densities.) The specific gravities of liquids and solids are their relative weights (masses) as compared with the weight (mass) of water at 4° C. as the unit. Other reference temperatures, for example, 15° C., are in use. For exact determinations the temperature of liquid and of water should be expressed.

A method largely used for determining the specific gravity of solids, particularly in respect of samples of woods, is that of weighing the volume of water bodily displaced and dividing the number so obtained into the weight of the body in air. A more exact method is that of weighing the solid body in air and then in water, subtracting the latter from the former and dividing the difference—that is, the weight of the water displaced—into the weight-in-air of the body.

For pharmaceutical purposes in Great Britain, the *British Pharmacopæia*, 1948, has introduced the absolute unit of density, namely, Weight per Millilitre, in place of the Specific Gravity. This is determined by weighing a known volume of liquid in a suitable pycnometer at 20° C., the volume of the pycnometer being determined from the datum that one litre of water at 20° C. weighs 997.18 grams when weighed against brass weights in air of density 0.0012 gram per millilitre. (See A.P.I. Scale, Densities, and Hydrometers.)

**SPECIFIC HEATS** — See Heat.

**SPECTROSCOPE and SPECTROSCOPY** — This is an instrument by means of which the light emitted by strongly heated substances can be examined. It is constructed of one or more prisms by which the coloured rays are separated and dispersed when light is made to pass through them. This analysis or splitting up of light into the different colours of which it is constituted furnishes what is termed the prismatic spectrum, each colour having its own peculiar refrangibility ranging from the red rays, which are the least refrangible, to the deep violet, which are most refrangible, at the other end of the rainbow. The term spectrum also includes the invisible regions on both sides of the visible region. A spectrum is also produced by passing light through a grating of glass having closely ruled lines on it. (See Mass-Spectrograph, and Wave Lengths.)

Various chemical salts, when heated in the blow-pipe or nearly colourless Bunsen-burner flame, impart characteristic colours indicative of

their nature, but where mixtures are concerned the indication is lost on account of the merging or blending of the various colours which takes place. Sodium compounds give a yellow colour to flame ; potassium salts tinge the flame purple ; whilst lithium salts communicate a crimson-red colour. The colour given by the salts of rubidium and cesium is indistinguishable by the naked eye from that of potassium compounds, but when these coloured flames are examined through the spectroscope the spectrum affords an easy and assured method of diagnosis, inasmuch as the chemical salts under examination furnish distinct bright bands of light. Sodium compounds give a distinct line or group of lines in the yellow (5,900 A.U., the D-line), lithium gives one band in the red (6,700 A.U.), and another in the yellow (6,100 A.U.), and potassium also gives two bands (one in the deep red and another in the violet), and when mixtures are examined, the individual or distinctive lines and bands are all respectively revealed. This method of detection is so delicate that so small a part as  $\frac{1}{180,000,000}$  grain of sodium salt and  $\frac{1}{8,000,000}$  grain of lithium can be detected. (15 grains=1 gram.) Characteristic spectra are afforded not only by substances which give colour to flame, but by every elementary body when heated to the degree at which its vapour becomes luminous.

Many of the elements were discovered by the use of spectrum analysis, including cesium, rubidium, thallium, indium, helium, and gallium, before anything was known of their chemical properties.

The spectroscope in its simplest form consists of a prism fixed upon a stand placed in line with a hollow tube provided with a slit or shutter at the end opposite to which the flame is placed for examination. The light under examination passing along this tube by way of the slit is received upon the prism through a lens fixed in the tube called the collimator, which renders the rays parallel, and the refracted rays from the red end to the blue end are received by the observer using the telescope, which is placed in such a position that the bent rays fall upon its lens, and are magnified by it. Otherwise, instead of using the eye, it may be replaced by a photographic plate or film (as in the spectrograph) on which the spectral bands are thus recorded.

"Emission spectra" can be produced in a number of ways, namely, by the use of flame such as that of a Bunsen lamp in respect of the more or less volatile metallic salts ; or by the electric arc, which furnishes a much higher temperature, the spectrum being obtained by placing the substances to be examined into the arc between the carbon poles ; or by means of the sparks from an induction coil made to pass between small poles of the substance, or discharged through gases—a method which can be applied to solutions ; or by the use of cathode streams for the production of phosphorescence in solid substances.

The relation between the powers of emission and those of absorption for rays of the same wave-lengths is constant for all bodies at the same temperature.

Organic solutions were first examined by photographing the spark spectrum of an alloy of tin, lead, cadmium, and bismuth, as obtained through a solution of the subject under examination.

The bright yellow sodium lines are made to appear as dark lines or spaces by allowing the rays of a white light (like that of the oxy-hydrogen flame or an incandescent platinum wire) to pass through a flame coloured by a sodium compound, and then to fall upon the slit of a spectroscope, because the yellow flame absorbs the same kind of light as it emits, and similarly each substance in the vaporous state has the power of absorbing the same rays as it emits, or being opaque to same. This accounts for the dark spaces or so-called "Fraunhofer" lines observed in the solar atmosphere, these being, as is believed, bright lines reversed, and indicative, therefore, of the presence in the sun's atmosphere of those substances which are capable of yielding the coincident bright lines, including iron, sodium, calcium, magnesium, chromium, barium, copper, zinc, hydrogen, and nickel.

By the investigation of emission and absorption spectra, using a variety of appliances adapted to the many different substances requiring examination, it has been found possible to acquire a very definite knowledge of the constitution of the sun's atmosphere, the fixed stars, and the so-called nebulae (which are regarded as masses of glowing gases). Working with a very large telescope, J. S. Plasket has obtained evidence of the presence of calcium and sodium vapours in the spaces between the stars and the earth, and some 58 elements have been identified in the solar spectrum, although the spectrum tells nothing respecting the composition of the body bulk of the sun and stars. "The hotter the star the simpler the spectrum, until at the highest temperature we obtain practically nothing but the lines of hydrogen or helium" (H. Dingle).

These various methods have also been turned to account for the identification of precious stones, dyes, and colouring matters; the detection of alum in wines and fruit juices, blighted wheat in flour, and blood-stains; the estimation of alkaloids, the detection of minute quantities of metals, the valuation of indigo samples, the examination of essential oils, sugar analysis, etc. The spectroscope has also proved of great value in the investigation of many organic compounds, radical groups such as  $\text{CH}_2$ ,  $\text{CH}_3$ ,  $\text{NH}_2$ ,  $\text{C}_6\text{H}_5$ ,  $\text{OH}$ , etc., all giving characteristic absorption bands. (See *Molecular Spectra and Molecular Structure* (The Faraday Society, London); Twyman and Smith's *Wave-length Tables for Spectrum Analysis* (Adam Hilger, Ltd., London); E. C. C. Baly's *Spectroscopy* (Longmans, Green and Co., London); *A Treatise on Light*, by R. A. Houston (Longmans, Green and Co., London); and *Introduction to Physical Optics*, by J. K. Robertson (Chapman and Hall, London).)

**SPECTRUM** — See Spectroscope, and Wave Lengths.

**SPECULAR IRON ORE (Red Hematite)** — See Iron.

**SPECULUM METAL** — An alloy of about 32 per cent. tin and the balance copper, used for reflectors and mirrors but largely superseded by silvered glass. It is also employed for the electrolytic coating of tableware to resist tarnishing.

**SPEISS COBALT** — See Cobalt.

**SPELTER** — A commercial name for zinc.

**SPENCE METAL** — Made by melting iron sulphide with sulphur in such proportions as to melt at about 320° F. ; used for making busts and medallions and as a jointing material for pipes, etc.

**SPENT OXIDE** — See Gas (Coal), and Sulphur.

**SPERM OIL** — See Fish Oils.

**SPERMACETI** — See Waxes.

**SPERMINE (Spermatin)** ( $C_{10}H_{26}N_4$ ) — A crystalline base (isolated as phosphate) from testes, ovary, spleen, pancreas, thyroid, thymus, brain, and distillers' yeast. Spermidine is the name given to a closely associated base.

**SPERRYLITE** — A rare mineral containing platinum diarsenide ( $PtAs_2$ ) occurring in Ontario, Wyoming, the Transvaal, etc. A sulpharsenide of platinum has been discovered containing 64.2 per cent. platinum, 9.4 per cent. palladium, 17.7 per cent. sulphur, and 7.7 per cent. arsenic.

**SPHAGNUM** — A club moss (*Sphagnum acutifolium*) which grows abundantly in bogs on peat moors. Sphagnum peat is stated to contain 40 per cent. humic acid.

**SPHALERITE (Black Jack)** — Mineral zinc sulphide or zinc blende.

**SPIKE OIL** — See Lavender (Spike) Oil.

**SPIKENARD (Nard)** — A perfume obtained in the northern part of India from *Nardostachys jatamansi*. The same name is given to other perfumes used as substitutes obtained from plants of the same N.O. growing in the Alps and other Southern European mountains.

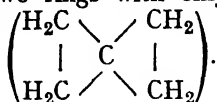
**SPINACENE** — See Shark Oil, and Squalene.

**SPINELLE (Spinel)** — A natural crystalline magnesium aluminate ( $MgO, Al_2O_3$ ), used as a gem and as an abrasive (crystal system No. 1, and sp. gr. 3.5). There are a number of varieties of different colours ; found in Ceylon and elsewhere ; varying also to some extent in composition.

**SPINTHARISCOPE** — Apparatus for viewing in the dark the scintillations or glints of light that are produced when an alpha-particle strikes a zinc sulphide screen.

**SPIRIT(S) OF WINE** — Ethyl alcohol, usually containing 90 volume per cent., which strength is often referred to as S.V.R. (Spiritus Vini Rectificatus).

**SPIRO COMPOUNDS** have two rings with only one carbon atom in common, *e.g.*, spiropentane



**SPODUMENE** — Lithium aluminium silicate ( $\text{Li}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$ ) containing about 8 per cent. lithium, found in California, etc.; crystal system No. 5, and sp. gr. 3.1 to 3.2.

**" SPONDITE "** — See Cellulose Acetate.

**SPONGES** (*Porifera*) are organisms of various species (found adherent to rocks in the Mediterranean and elsewhere), the tissues of which, constitutionally, are, from a chemical point of view, nearly related to the fibroin of silk. *Spongia* from *Hippospongia equina* is stated by V. J. Clancey to yield, upon hydrolysis, mainly glutamic acid and glycine, with smaller quantities of leucine, aspartic acid and other substances.

**SPONGY PLATINUM** — See Platinum, and Catalysis.

**SPONTANEOUS COMBUSTION** ensues as a result of the development of heat arising from chemical changes; thus, cotton waste soaked in linseed oil will sometimes fire in consequence of the rapid oxidation of the oil. Coal will sometimes pass into spontaneous combustion, due to fineness of condition and its "reactive" constituents, namely, those convertible into alkali-soluble ulmins by mild oxidation. Similarly, phosphorus exposed to the air will take fire, and burnt lime during slaking with water develops enough heat to fire wood that may happen to be in close contiguity.

**SPRAY DRYING** — See Drying.

**SPRAYS** — See Insecticides, and Wetting Agents.

**SPRENGEL PUMPS** — See Pumps.

**SPRUCE OIL** — The volatile oil distilled from the leaves and twigs of *Picea alba* and *P. nigra*, containing pinene, cadinene, and bornyl acetate; soluble in alcohol and ether; sp. gr. about 0.900 at 15° C.; opt. rot. —22° to —25° at 20° C. Used in perfumery.

**SQUALENE** ( $\text{C}_{30}\text{H}_{50}$ ) — An aliphatic dihydrotriterpene, occurring in oils from certain fish livers, and related in constitution to the carotenoids. (See Bloomfield (*Rubber Chem. and Technol.*, 20, 360 (1947).))

**SQUALUS LIVER OIL** — See Fish Oils.

**SQUILL** — The dried bulb of *Urginea maritima* (Linn.) Baker (*Urginea scilla* Steinh.), divested of its outer membranous covering, cut into slices and dried. It is indigenous to the Mediterranean region and contains a number of bitter glycosides including scillaren A and scillaren B. These glycosides are related to the cardiac glycosides of

digitalis, but squill is used in medicine mainly as an expectorant. Red squill, derived from a red variety of *Urginea maritima*, contains xanthoscllid and is used as a rat poison. (See *Digitalis and Other Cardiotonic Drugs*, by E. R. Movitt (Oxford Medical Publications, New York).)

“**STABILARSAN**” — An anti-syphilitic product of glucoside character, soluble in water, and which hydrolyses with precipitation of arsphenamine base. (See Arsphenamine.)

**STAINLESS STEEL** — See Rustless Iron and Steel.

**STAIN REMOVAL** — Stains may be more or less removed from materials by various means of a physical and chemical nature. Where solids are concerned attrition with kieselguhr, rubber, bread, or pumice stone, etc., will sometimes remove surface deposits; in other cases of a greasy character, solvents can be employed, such as alcohol, petrol, turpentine, and carbon tetrachloride, regard always being had to the nature of the stains; while in yet other instances, the removal must be based upon consideration of chemical reactions.

Ordinary ink stains can be removed from certain materials by the use of oxalic acid solution; fruit stains by the use of hydrogen peroxide or sodium hydrogen sulphite; iodine stains by sodium thiosulphate; grass stains by alcohol; rust stains on cloth by the solvent action of solutions of magnesium and sodium fluosilicate, by immersion in the warm fluid of 3 to 6 per cent. strength, followed by immediate rinsing in hot water and subsequent passage through a dilute solution of sodium carbonate. Verdigris stains on cloth may be removed by saturation with ammonia, rubbing with a cloth soaked in ammonia, and treatment with a hot solution of potassium fluoride, or a cold solution of dilute hydrochloric acid.

**STALACTITES** — Deposits of calcium carbonate like icicles, formed by dripping water from the roofs of calcareous caves, due to evaporation of water and the escape of carbon dioxide from the solution of calcium carbonate dissolved in water and previously held in solution by its agency.

**STALAGMITES** — Similar deposits to stalactites growing upon the floor of caves out of the water dropped from above (by evaporation).

**STALAGMOMETER** — Instrument for measuring surface tension (see same) by the drop method.

**STANDARD SOLUTIONS** — See Reagents, and Volumetric Analyses.

**STANDARD SPECIFICATIONS** — A number of these are issued by the B.S.I. (B.E.S.A.), London, applicable to cements, coal, coke, steel cylinders, solders, ebonite, chemical lead, road-tars, forgings, castings, lead, white spirit, paints, regulus metals, bronze A, various steels, turpentines, colours, lubricating and other oils (used for paint-making and varnish) viscosity, etc. Many specifications (1,500) and an index are available. The International Standards Association promulgates

numerous standard specifications in the field of engineering. In the United States the principal agencies of this kind are American Society for Testing Materials, and American Standards Association. The American Chemical Society has published numerous specifications for reagent chemicals (*Ind. Eng. Chem.*, **17**, 756 (1925) ; **18**, 636, 759 (1926) ; **19**, 645, 1369 (1927) ; **20**, 979 (1928) ; *Ind. Eng. Chem., Anal. Ed.*, **1**, 171 (1929) ; **2**, 351 (1930) ; **3**, 221 (1931) ; **4**, 154, 347 (1932) ; **5**, 289 (1933) ; **12**, 631 (1940) ; **16**, 281 (1944) ; *Anal. Chem.*, **19**, 210 (1947). The American Petroleum Institute is active in the field related to petroleum and its products. Many of the purchases of the United States Army and Navy are made upon specifications publicly announced by each.

**STANDARDS (Analytical)** — The United States Bureau of Standards issues a number of standard analysed materials, and distributes a price list of these.

**STANDARD TEMPERATURE AND PRESSURE (for Gases)** — Standard conditions for gases are temperature 0° C., pressure 760 mm. of mercury, and dry. (See Vapour Pressure, and Water.)

**STANNATES** — See Tin (Compounds).

**STANNIC ACID** — See Tin (Compounds).

**STANNITES** — See Tin (Compounds).

**STAR-ANISE OIL** — See Aniseed Oil.

**STARCH (Amylum)** is a carbohydrate reserve of all angiospermic plants, occurring as grains in the leaves, stems, etc., but mainly in the reserve food organs, such as roots, tubers, corms, etc. It is most abundant in wheat, maize, barley, oats, rice, and potatoes. The shapes of the starch grains vary greatly from plant to plant and constitute a means of identification of the plant in crushed or powdered form.

Chemically, starch is a polysaccharide of the formula  $(C_6H_{10}O_5)_n$  and on boiling with acids is converted completely to glucose ; hydrolysis with maltase converts it in 80 per cent. yield to maltose. It may be defined as the naturally occurring *alpha*-glucopyranoside polymer found in the plant kingdom as minute granules that are insoluble in cold water and birefringent under polarized light. Corn-starch granules are small (diameter 10-25 microns) and often polygonal in shape ; potato-starch granules are large (diameter 15-100 microns), oval in shape, and with oyster-like striations ; and tapioca-starch granules are also oval and frequently cup-shaped or truncated.

The molecular weight of starch is extremely high, but the figure obtained varies according to the method employed. Although unaffected by cold water, starch is converted to a gel by boiling with water, the well-known mucilage of starch. It has been shown that the addition of amyl alcohol to the latter under the right conditions causes the precipitation of amylose, one of the two constituents of

starch, occurring to the extent of about 28 per cent. Analysis of amylose shows it to consist of about 300 glucose units, arranged in a chain; this is verified by the fact that amylose can be obtained in threads and sheets, just like cellulose.

The other constituent of starch, amylopectin, has a more complicated structure, being in the form of two-dimensional sheets, each molecule built up of about 3,000 glucose units. Amylopectin has been synthesized.

Potatoes contain from 17 to 27 per cent. of starch, wheat from 50 to 75 per cent., barley and oats about 60 per cent., maize about 67 per cent., and rice about 76 per cent.

**Soluble starch** is prepared by the partial hydrolysis of starch, but the hydrolysis has to be carefully controlled, else the hydrolysis is carried too far and the product no longer gives the well-known blue colour with iodine.

**Dextrine** is prepared by heating dry starch for some hours at 200° C. It dissolves readily in cold water to form "British gum," an adhesive used for postage stamps; it is also used for calico-printing.

By acetylation, starch can be converted into a number of so-called **acetates**, which, like amylose acetate itself, can be obtained in the form of films or sheets. *Sago* is a starch produced from the pith of the stems of the sago palm; **tapioca** and **cassava** are made from *Jatropha manihot*; arrowroot is prepared from species of Maranta, and has been used as a binder for briquettes and in medicine. *Lichenin*, or *moss-starch*, is contained in many lichens, including Iceland moss, and is probably identical with amylose.

Starch in various forms is used in laundering for glazing linen and the finishing of textiles; also as a filler in compounding cocoa preparations, the manufacture of adhesives, explosives, invalid foods, as a binder, and as a lubricant and burster in the manufacture of medicinal tablets.

(See *Introduction to the Chemistry of Carbohydrates*, by Honeyman (Clarendon Press, Oxford); *A Comprehensive Survey of Starch Chemistry*, by R. P. Walton (Reinhold Publishing Corp., New York); *Starch: Its Chemistry*, by L. Eynon and J. H. Lane (W. Heffer and Sons, Cambridge); *Chemistry and Industry of Starch*, by Ralph W. Kerr (Academic Press, New York); "Determination of Starch in Cereal Products," by Herd and Kent-Jones (*J.S.C.I.*, **50**, 15T) (1931); "Action of Amylase on Starch," by H. C. Gore (*Ind. Eng. Chem.*, **28**, 86 (1936)); also Beer, Carbohydrates, Glucose, Potatoes, Rice, and Wheat.)

**STASSFURT SALTS** — The dried-up residue of a great prehistoric ocean, containing from 9 to 15 per cent. pure potash, and utilized for the preparation of various potassium salts. (See Carnallite, Sylvine, Kainite, Kieserite, and Potassium.)

**STATES OF MATTER** — See Matter.

**"STAYBRITE"** — A make of acid-resisting rustless metal (chromium-nickel steel) having a yield-point of 15 to 17.5 tons per square inch.

The carbon content in the standard material is about 0.30 per cent., so that it hardens well, while the specific gravity is slightly less than that of mild steel, varying with grades from 7.726 (a hard variety) to 7.925 (a soft variety). The mechanical, physical, and corrosion-resisting properties of the several varieties are described in the manufacturers' publications. In certain makes proportions of tungsten and silicon are added to impart additional strength at high temperatures.

**STEAM** — Steam is used to generate power and to supply heat. For power generation it is required at medium or high pressure and is generally superheated; for heating, low-pressure saturated steam is preferred. Often, however, the same steam can be used for both purposes. For example, steam may be raised at 650 pounds per square inch, superheated, and fed to turbines generating electrical power; passed out from the turbines at 150 lb. per sq. in. and used to drive reciprocating steam pumps; exhausted from the pumps at 15 lb. per sq. in. and passed to steam heating coils and jackets. Provided that the successive loads are reasonably near to being equal, a considerable overall economy is effected.

The thermodynamic properties of steam at different temperatures and pressures are given in steam tables such as those of J. H. Keenan and F. G. Keyes (John Wiley and Sons, New York); or G. S. Callender and A. Egerton (Edward Arnold and Co., London). The latent heat of steam at 212° F. is 970 British Thermal Units per pound or 539 calories per gram.

Steam boilers are of two types, fire-tube and water-tube. Small boilers are generally of the former type, consisting of a cylindrical shell pierced by tubes through which the combustion gases pass. Larger boilers have steam and water drums connected by a great many tubes within which water is evaporated. The efficiency of steam boilers is expressed as the percentage of heat contained in the fuel which is recovered in the steam. Typical figures are:

Type of Boiler	% Efficiency
Small fire-tube, no economizer .. .. .	55
Small water-tube with economizer .. .. .	60
Large fire-tube with economizer .. .. .	65
Large water-tube with economizer .. .. .	70
Large central station .. .. .	80-85

As a source of heat, saturated steam has the advantages of low cost, high heat content per lb., high rate of heat transfer, heat liberated at constant temperature. These qualities make it an ideal heating medium for many process purposes. When pure saturated steam condenses on an ordinary metal surface, film coefficients of heat transfer ranging from 700 to 5,000 B.Th.U./sq. ft./° F./hr. are obtained, depending on the rate of condensation per unit area and the shape and orientation of the surface. If, however, the metal surface is coated with a trace of a substance such as oleic acid which prevents the

condensate from wetting it, then "dropwise" condensation occurs and coefficients up to 18,000 B.Th.U./sq. ft./° F./hr. are obtained. These coefficients are greatly reduced by the presence of even a fractional percentage of air or non-condensable gas in the steam.

When steam is used for heating by means of closed coils or jackets, provision must be made to (a) remove the condensate as soon as it is formed, (b) prevent air from accumulating in the steam space. The former duty is performed by steam traps (of which there is a great variety), and the latter duty by suitably located air vents. The proper choice and installation of traps and air vents is very important if steam is not to be wasted.

*References:* Croft and Purdy, *Steam Boilers* (McGraw-Hill Book Co., New York); O. Lyle, *The Efficient Use of Steam* (H.M. Stationery Office, London, 1947); L. G. Northcroft, *Steam Trapping and Air Venting* (Hutchinson, London); H. N. Bassett, *The Chemical Technology of Steam-Raising Plant* (Edward Arnold and Co., London); W. H. McAdams, *Heat Transmission* (McGraw-Hill Book Co., New York).

**STEARIC ACID** ( $C_{17}H_{35}COOH$ ) — A solid member of the normal fatty acids present in most animal and vegetable fats and oils, and generally associated in varying proportions with palmitic and oleic acids, all in combination with glycerol in the form of glycerides. It is most abundant in the more solid fats and forms hard soap when saponified, setting free the glycerol, as explained elsewhere. (See Soaps.) It can be readily prepared from beef or mutton fat, and when pure is white, crystalline, of sp. gr. 0.847 at its m.p. 69° C.; is soluble in alcohol and ether, and used in making soaps and candles and as a softener for rubber goods.

Exposed to oxygen in presence of manganese stearate at 120° to 130° C., volatile acids, including acetic, formic, and butyric acids, are produced to some extent. The main oxidized product after washing has been found to have acid value 206 and sap. v. 244, and to contain some proportion of lactones (Salway and Williams).

The ammonium, potassium, and sodium soaps of stearic acid form solid creams, even in 5 or 10 per cent. solutions in water, and such creams form the base of vanishing creams used in the cosmetics industry; on rubbing into the skin, the cream "vanishes" due to the evaporation of the water, leaving a thin film of stearate. The sheen on certain creams is due to a slight excess of stearic acid, which crystallizes out in a characteristic manner on cooling.

Certain metallic stearates, such as those of calcium and aluminium, are recommended for use as metallic soaps, also as diluting agents in preference to hydrated lime, for admixture with Paris green as used for dusting to prevent the maturing of malaria-carrying mosquitoes. These compounds increase the floating power of the Paris green when used as dusting powder on water in pools and ponds. Some metallic stearates also find use as special lubricants and as driers and flatteners in paints and varnishes. (See Fats, and Soaps (Metallic).)

**STEARIN (Stearine, Tristearin)** ( $C_3H_5(OOCC_{17}H_{35})_3$ ) — The glyceride or glyceryl ester of stearic acid, occurring as a solid constituent of fats, and yielding potassium stearate (soap) and glycerol upon saponification with alcoholic potash. Beef stearin melts at  $71^\circ C.$ , has a sp. gr. 0.862, and is soluble in ether, chloroform, and carbon disulphide. Other commercial stearins have melting points up to  $120^\circ C.$ , the melting-point being largely dependent upon the proportion of the stearic acid content. They are largely used in soap and candle making, also in the leather and tanning trades and in making polishes. A residual pitch, known as stearin pitch, is obtained by the distillation of fatty acids. (See Fats).

**STEAROPTENES** — The solid constituents of certain essential oils, the liquid parts being designated *eleoptenes* or *oleoptenes*.

**STEATITE (Soapstone)** — A form of talc, found in many countries, slabs of which are often used for making firestones in furnaces and stoves, and in compressed powder form for making sparking-plugs. It is mechanically stronger than stoneware and can be machined with greater accuracy. It is also used for making electrical insulators, acetylene burners, in porcelain manufacture, and by tailors to mark cloth. (See French Chalk, Soapstone, and Talc.)

**STEEL** — See Iron, and Rustless Iron.

**STEFAN-BOLTZMANN LAW** — See Heat Transfer.

“**STELLITE**” — Trade-mark for non-ferrous alloys of cobalt, chromium, and tungsten used for metal-cutting tools, hard-facing welding rod, and metal parts requiring resistance to heat, wear, and corrosion. (See Cobalt.)

“**STENOL**” (Du Pont) — Trade-mark for stearyl alcohol. Used as an emulsifier, antifoaming agent, lubricant, and chemical raw material.

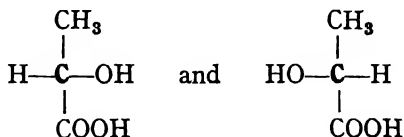
**STEPHANITE** ( $5Ag_2S, Sb_2S_3$ ) — A native sulphantimonite of silver (crystal system No. 4, and sp. gr. 6.26) occurring in Freiburg, the Harz, Hungary, Colorado, Nevada, etc.

“**STERAMIDE**” — See Sulphacetamide.

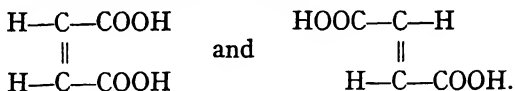
**STERCULIA OIL** from members of the *Sterculiaceæ*, N.O. Columniferae, such as the *S. chica* and *S. lasiantha* of Brazil, yielded by both pericarp and kernel; the skin and pulp giving nearly 27 per cent., and kernels about 29 per cent. The pulp oil has a sp. gr. at  $100^\circ/15.5^\circ C.$  of 0.8561; sap. v. 191.2; and i.v. (Wijs) 69.7. The kernel oil has a sp. gr. of 0.8675, sap. v. 180.2, and i.v. 62.3.

**STEREOCHEMISTRY (Stereometry, Chemistry in Space)** — The study of the relative positions occupied in space by atoms or groups in molecular bodies. (See Turner and Harris, *Quart. Reviews*, London, 1, 229 (1948); *Stereochemistry*, by A. W. Stewart (Longmans, Green and Co., London); also Co-ordination, Formulas, Isomerism, Rings, Stereoisomerism, and X-Rays.)

**STEREISOMERISM** — The isomerism exhibited by two or more compounds which are structurally identical and differing only in the arrangement of the constituent atoms in space. There are two forms of such isomerism, namely, (1) optical isomerism, caused by the presence in the molecule of one or more assymetric carbon atoms (rarely an atom other than carbon) and giving rise to optical activity; and (2) geometrical isomerism, resulting from the presence of a double bond in the molecule, which gives rise to two spatially different forms, but does not produce optical activity. An example of (1) is dextro- and lævo-lactic acid,

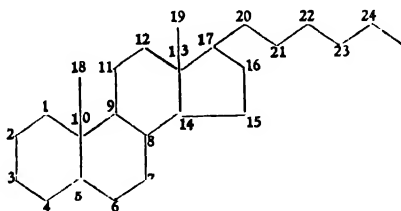


and of (2) is maleic and fumaric acids,



(See Isomerism.)

**STEROLS** — A group of high molecular weight alcohols, occurring either free or combined, widely distributed in animal fats, vegetable oils, yeast cells, bile, etc. They, like the saponins, cardiac glycosides, and bile acids, contain the tetracyclic ring system of cyclopentano-phenanthrene, which for ease of description is numbered as follows:



Except when otherwise indicated by double bonds, all the four rings are fully reduced and are not aromatic, but there are usually one or more double bonds in the ring system. Cholesterol ( $\text{C}_{27}\text{H}_{45}\text{OH}$ ) is the 3-hydroxy, 5(6)-ene, and 17- $\text{CH}(\text{CH}_3)(\text{CH}_2)_3\text{CH}(\text{CH}_3)_2$  derivative of the sterol skeleton.

Cholesterol is the principal sterol of the animal organism, but occurs also in large amounts in wool-fat. Ergosterol ( $\text{C}_{28}\text{H}_{49}\text{OH}$ ), obtained from yeast, is the 3-hydroxy, 5(6), 7(8)-diene, and 17- $\text{CH}(\text{CH}_3)\text{CH}:\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$  derivative of the sterol skeleton. Stigmasterol ( $\text{C}_{29}\text{H}_{47}\text{OH}$ ), found in calabar and soya beans, is the 3-hydroxy, 5(6)-ene, and 17- $\text{CH}(\text{CH}_3)\text{CH}:\text{CH}(\text{C}_2\text{H}_5)\text{CH}(\text{CH}_3)_2$  derivative of the sterol skeleton.

Since the reduced ring system of the sterols can exist in 512 stereoisomeric forms the distinction of one sterol from another would prove an almost insurmountable task, were it not for the remarkable consistency of the ring-system structure in the natural products. In fact, the only natural stereochemical variation exists at carbon atom 5, the *cis* compounds being known as the "normal" series, simply because this configuration is normal to the bile acids, whereas those compounds having the *trans* configuration at carbon atom 5 are said to belong to the "allo" series.

**Bile Acids** differ mainly from the sterols in having a short chain in position 17, ending in a COOH group, and in having more hydroxyl groups in the molecule. These acids are usually found combined with one of the amino-acids, glycine or taurine, the commonest ones being known as taurocholic acid and glycocholic acid respectively, both being hydrolysed to yield cholic acid and, respectively, taurine and glycine. Cholic acid ( $C_{23}H_{38}(OH)_3COOH$ ) is the 3, 7, 12-trihydroxy and 17-CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>2</sub>COOH derivative of the sterol skeleton.

**Sex Hormones** have usually only a ketone or secondary alcohol group in position 17, but the left-hand ring is aromatic.

**Saponins and Cardiac Glycosides** have more complicated groupings in position 17, usually an unsaturated butyrolactone ring.

Various members of the vitamin D family are sterols, and occur, with other sterols, in the unsaponifiable part of fish-liver oils. All oils and fats contain a small percentage of unsaponifiable matter, which consists mainly of sterols and other alcohols of high molecular weight.

See *Natural Products Related to Phenanthrene*, by Louis and Mary Feiser (Reinhold Publishing Corp., New York); *Organic Chemistry*, by Paul Karrer (Elsevier Publishing Co., New York); Bile, Digitalis, Hormones, and Saponins.

**STIBILITE** — A native oxide of antimony (crystal system No. 5).

**STIBNITE (Grey Antimony, Antimony Blende)** — Mineral antimony sulphide ( $Sb_2S_3$ ); crystal system No. 4, and sp. gr. 4.5. (See Antimony.)

**STIBOPHEN ("Fouadin")** ( $C_{12}H_4O_{16}S_4SbNa_5 \cdot 7H_2O$ ) — A colourless, crystalline powder, namely, sodium-antimony-bispyrocatechol-3,5-sodium disulphonate; soluble in water, insoluble in ether, chloroform, and acetone. It contains about 15.8 per cent. of antimony and is used in medicine for the treatment of tropical diseases.

**STICK LAC** — See Shellac.

**STILBENE (sym.-Diphenylethylene)** ( $C_6H_5 \cdot CH : CH \cdot C_6H_5$ ) — A nearly colourless, crystalline body of m.p. 124° C. and b.p. 306° C. prepared by the action of sodium upon benzyl dichloride ( $C_6H_5CHCl_2$ ) or by passing toluol over heated lead oxide. It is soluble in alcohol and ether. Certain of its derivatives are used in the dye industry, and others are employed in medicine as synthetic oestrogens.

**STILBITE** — A mineral, hydrated silicate of calcium and aluminium of zeolite character ( $Na_2Ca$ )O,  $Al_2O_3$ ,  $6SiO_2$ ,  $6H_2O$ ; crystal system No. 5, and sp. gr. about 2.0.

**STILBŒSTROL** ( $C_{18}H_{20}O_2$ ) — A colourless, crystalline powder, namely, 4,4'-dihydroxy- $\alpha,\beta$ -diethylstilbene; sparingly soluble in water; soluble in alcohol and ether and in aqueous solutions of alkali hydroxides; m.p.  $168^\circ$  to  $171^\circ$  C. Stilbœstrol possesses a physiological action similar to that of the female hormone, œstrone, and is used in medicine for the treatment of conditions due to hormonal deficiency in the female. For a review of the synthetic œstrogens, see E. C. Dodds in *J. Pharm. et Pharmacol.*, **3**, 137 (1949). (See Dienœstrol, and Hexœstrol.)

**STILLS** — See Distillation, and Retorts.

“**STOCKALITE**” — A proprietary brand of colloidal clay as required for use in rubber, paint, and toilet articles industries.

**STOCKHOLM TAR** — A tar of several grades distilled from the resinous wood of the pine, and largely used in connection with wooden ship-building for caulking, tarring ropes, making roofing compounds, and preserving timber. It is soluble in turpentine.

**STOICHIOMETRY (Chemical Mathematics)** deals with the numerical relationships of atoms and molecules of chemical bodies, their interactions, and the changes of energy involved. (See *Stoichiometry*, by Sidney Young (Longmans, Green and Co., London); *Industrial Stoichiometry*, by W. K. Lewis and A. H. Radasch (McGraw-Hill Book Co., New York); *Industrial Chemical Calculations*, by O. A. Hougen and K. M. Watson (John Wiley and Sons, New York); *Chemical Calculations*, by J. S. Long and H. V. Anderson (McGraw-Hill Book Co., New York); *Physico-Chemical Calculations*, by Joseph Knox (D. Van Nostrand Co., New York); *Chemical Process Principles*, by O. A. Hougen and K. M. Watson (John Wiley and Sons, New York).)

**STOKES' LAW** — See Sedimentation.

**STONE** — For constructional purposes, stone of various kinds is required for frontages, dressings, and some classes of engineering work; for random blocks and rubble; for use in making concrete pavements and roads; as slates for roofing, etc., and for calcination in making lime and cement. Among the kinds largely used are the carboniferous and triassic formations of hard and soft varieties of sandstone, which abound in Yorkshire, Lancashire, Cheshire, and elsewhere; the jurassic system of rocks, which furnish the best Portland stone and the softer Bath stones.

The carboniferous limestones yield also a closer-grained and heavier type, such as the Hopton Wood stone of Derbyshire. The somewhat similar but older limestone of Devon; the magnesium limestones of Derbyshire, Notts, and Yorkshire; the Ragstone of Kent; the warm brown stone of Nutfield, and the fine granites of Cornwall, Devon, Westmorland, and Scotland, are others among many varieties of stone found in Great Britain.

Sales of dimension stone in the U.S.A. are per annum of the order of \$9,000,000 for granite, \$5,000,000 for marble, \$2,500,000 for limestone, and \$700,000 for sandstone. The principal producing states are

Georgia, Indiana (limestone), Maine, Minnesota, Missouri, New Hampshire, New York, Ohio (sandstone), South Dakota, and Vermont. The corresponding value of limestone for fluxing and metallurgical purposes (not Portland cement) is \$25,000,000.

**STONE PRESERVATION** — Among film applications used in respect of buildings are sodium silicate, silicic acid esters, and gelatinous solutions (followed by spraying with formaldehyde to fix same). Creosote and many other preparations, which will cover the surfaces with a practically insoluble coating, may also be used according to circumstances.

The "Fluoridation" method employs soluble fluorine salts which are said to leave the surfaces impervious to water and resistant to acidity of the atmosphere; zinc and magnesium fluosilicates being among the agents employed.

In the United States resort is frequently made to the use of wax or a stearate dissolved in a volatile solvent applied with a brush or spray.

A. P. Laurie has experimented with silicic acid ester which mixes readily with volatile solvents, and when exposed to air and moisture, deposits hydrated silica in transparent layers as an efficient preservative to stone.

Attrition (brought about by wind, water, and changing temperatures) is the most potent destructive agent, while water acts as a bursting agency by freezing within the pores of stone and as a solvent in proportion as it contains sulphur oxides in solution. Carbon dioxide contained in air and water is also destructive, particularly of limestone, as it leads to the formation of soluble calcium hydrogen carbonate.

From chemical considerations it does not appear likely that bacterial action can have any material influence in stone decay, although some attention has been paid to this subject with a more or less negative result. Alkaline washes (lime, potash, soda) are useful in giving some protection against attack by acids in the atmosphere.

**STONEWARE** is largely used in chemical industries. (See Porcelain, and Refractories.)

**STORAGE BATTERIES** — See Electricity.

**STORAX (Styrax)** — See Balsams, and Styrene.

"**STOVAINE**" — See Amylocaine.

"**STOVARSOL**" — See Acetarsol.

**S.T.P.** — Standard temperature and pressure. (See Normal Temperature.)

**STRAIN THEORY** — The four valencies of the carbon atom are, in the normal state, directed to the four corners of a regular tetrahedron, the carbon atom being regarded as being at the centre of the tetrahedron. When two or more of the valencies are forced out of this normal arrangement, by the formation of a ring or a double bond, then a strain is set up, and instability results in the molecule. In the unstrained state the angle between any two valencies is  $109^{\circ} 28'$ , and it can thus be seen that in carbon rings containing 2, 3, or 4 atoms, in which the angles between any two valency bonds are respectively 0,

60, and 90 degrees, the strain will be considerable. This is the reason for the instability of such compounds. Five-membered carbon rings are therefore more stable, having an inter-bond angle of  $108^\circ$ . In the case of rings having six or more atoms the planar arrangement is no longer the rule, as the ring is capable of becoming buckled so that the valency bonds between any two carbon atoms can always be  $109^\circ 28'$ , and hence large rings, when formed, are quite stable. (See article on the "Strain Theory" in Perkin and Kipping's *Organic Chemistry* (W. and R. Chambers, London).)

**STRAMONIUM** — The dried leaves and flowering tops of *Datura Stramonium* and *D. Tatula* (Fam. Solanaceæ). It contains from 0.3 per cent. to 0.5 per cent. of total alkaloids, consisting chiefly of hyoscyamine with small amounts of atropine and hyoscyne. It is used in medicine as an antispasmodic, particularly for the treatment of asthma. (See Atropine, Belladonna, and Hyoscyamus.)

**STRATOSPHERE** — The region that begins about 7 miles above the earth's surface and extends to an unknown height, is of uniform temperature of about  $-55^\circ\text{C}$ . ( $-67^\circ\text{F}$ .), and in which there are no clouds, no storms, and very little wind. The stratosphere balloon, Explorer II, was used to collect samples of air up to 70,000 feet, and the samples showed practically no change in the ratio of nitrogen to oxygen from that at the surface of the earth. In the stratosphere there is relatively more ozone than near the earth. The layer of ionized air, called the ionosphere, appears to vary from 100 to 400 miles in height above the earth.

**STRAW** — A published ultimate analysis of straw is as follows: carbon 35 per cent.; hydrogen 5 per cent.; oxygen 38.5 per cent.; nitrogen 0.5 per cent.; water 16.5 per cent.; and ash 5 per cent. Apart from its other uses, straw, in the form of plaited rope, forms an excellent protective covering for waterpiping against frost, and is also used in making straw-board for cheap box-making. (See Feeding Stuffs, and Sewage.)

**STRENGTH, COMPRESSIVE** — For bricks and building stones the following data are approximately correct:

	Pounds per Square Inch			
Sand-lime brick .. .. .	..	..	..	3,500
Common brick .. .. .	..	..	..	4,000
Hard-burned brick .. .. .	..	..	..	8,000
Paving brick .. .. .	..	..	..	10,000
Sandstone .. .. .	..	..	..	9,000
Limestone .. .. .	..	..	..	9,500
Marble .. .. .	..	..	..	12,500
Slate .. .. .	..	..	..	14,000
Granite .. .. .	..	..	..	19,000
Trap rock .. .. .	..	..	..	20,000
Common brick				
In lime mortar .. .. .	..	..	..	550
In cement mortar .. .. .	..	..	..	900

**STRENGTH, TENSILE** — For some of the metals and alloys the following approximate data are presented :

	Pounds per Square Inch
Aluminium, 99·7 per cent. . . . .	55,000
Aluminium, 99·2 per cent. . . . .	12,000
Aluminium, 95 per cent. Al, 5 per cent. Si . . . . .	19,000
Copper, 99·9 per cent. . . . .	32,000–35,000
Copper, hard drawn . . . . .	50,000–67,000
Gold . . . . .	20,000
Iron, wrought, annealed . . . . .	40,000–50,000
Iron, 98·5 per cent., cast . . . . .	48,000
Iron (see Steel below)	
Lead, 99·92 per cent. Pb, 0·08 per cent. Cu . . . . .	1,740
Lead, hard . . . . .	3,100
Magnesium . . . . .	33,000
Nickel, 99·5 per cent. . . . .	65,000–140,000
Palladium . . . . .	39,000
Platinum . . . . .	32,000
Silver . . . . .	42,000
Tantalum, 99·5 per cent. . . . .	130,000
Tin . . . . .	4,000–10,000
Tungsten, drawn . . . . .	500,000
Zinc . . . . .	4,000–36,000
Brass, annealed . . . . .	40,000
Brass, hard drawn . . . . .	78,000
Bronze, hard drawn . . . . .	71,000
Bronze, aluminium, 90 per cent. Cu., 10 per cent. Al . . . . .	
Constantan, 60 per cent. Cu, 40 per cent. Ni . . . . .	120,000
Copper with Al and Fe . . . . .	Up to 100,000
Copper with Sn and P . . . . .	Up to 135,000
German silver, 18 per cent. Ni . . . . .	150,000
Gun metal . . . . .	25,000–50,000
Manganese bronze . . . . .	65,000–85,000
Monel metal . . . . .	65,000–170,000
Nichrome . . . . .	150,000
Phosphor bronze . . . . .	36,000–40,000
Steel, 0·08–0·15 per cent. C . . . . .	50,000–60,000
Steel, 0·15–0·30 per cent. C . . . . .	60,000–70,000
Steel, 0·30–0·50 per cent. C . . . . .	70,000–80,000
Steel, 0·55–0·75 per cent. C . . . . .	100,000–115,000
Steel, chromium . . . . .	Up to 250,000
Steel, 3·5 per cent. Ni . . . . .	100,000–120,000
Steel, manganese . . . . .	230,000

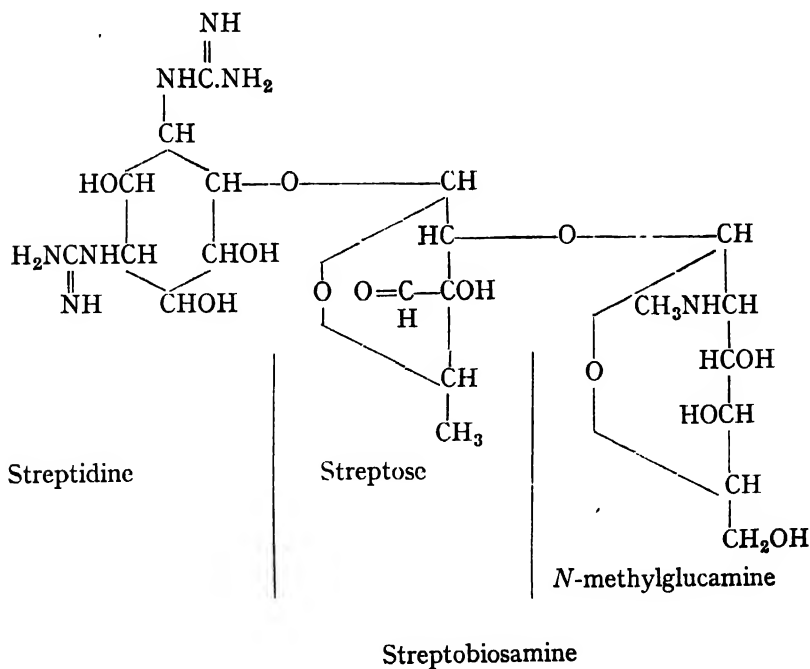
“ **STREPTOCIDE** ” — See Sulphanilamide.

**STREPTOMYCIN** — An antibiotic substance produced during the growth of *Streptomyces griseus* and first demonstrated in the culture filtrates by Waksman *et al.* in the United States in 1943. The organism is a

member of the Actinomycetes, an order of micro-organisms considered to be intermediate between the bacteria and moulds. Only certain strains of *Streptomyces griseus*, grown under suitable conditions, will produce streptomycin. The large-scale method of manufacture by deep culture is similar to that developed for the production of penicillin.

Streptomycin is of particular value since it is active against Gram-negative organisms which are not attacked by penicillin. They include *Mycobacterium tuberculosis*, *Hæmophilus influenzae* (Pfeiffer's bacillus), *Klebsiella pneumoniae* (Friedlander's bacillus), *Pasteurella tularensis*, *Escherichia coli*, *Proteus vulgaris*, *Pseudomonas pyocyanea* and *Aerobacter aerogenes*. Streptomycin is also effective against Gram-positive organisms and can be used for the treatment of conditions due to strains of organisms which have developed a resistance to penicillin, e.g., certain strains of the gonococcus.

Streptomycin is a complex organic base, containing glycosidic linkages in addition to basic amino groups. Unlike penicillin, it contains no sulphur. It is considered to be composed of a cyclic group, streptidine, attached to a disaccharide, streptobiosamine (which is itself composed of streptose and *N*-methylglucamine). Streptomycin has the empirical formula  $C_{21}H_{39}O_{12}N_7$ , and has been allotted the following structural formula :



The above formula has been ascribed to Streptomycin A, and a second compound, Streptomycin B, has also been isolated having an

additional molecule of mannose. Streptomycin B or mannosido-streptomycin possesses only one-quarter of the activity of streptomycin A.

For clinical purposes, streptomycin has been used in the form of its sulphate, hydrochloride, and calcium chloride complex. The normal salts are not readily crystallized from solution, and the calcium chloride complex, having the formula,  $C_{21}H_{39}O_{12}N_7 \cdot 3HCl(CaCl_2)_4$ , is the salt now most commonly used. The impurities present in crude preparations are liable to produce serious toxic reactions when used clinically and the purification of streptomycin is therefore an important consideration.

Preparations of streptomycin are assayed by a microbiological method and an arbitrary unit (S unit) has been fixed. One gram of streptomycin base (or 1.3 grams of calcium chloride complex) is equivalent to 1,000,000 S units.

On oral administration, streptomycin is not absorbed from the gastro-intestinal tract and for systemic therapy must be given by injection. Streptomycin is of value only in certain forms of tuberculosis and is supplementary to other established forms of treatment. Favourable reports have been made of the use of streptomycin for the treatment of tularæmia, urinary tract infections due to Gram-negative organisms and other conditions.

Dihydrostreptomycin is prepared by hydrogenation of streptomycin, and involves the conversion of the aldehyde group in the streptose fragment into a primary alcohol. Dihydrostreptomycin is used either as the sulphate of hydrochloride and has a lower toxicity than streptomycin.

The output of streptomycin in the U.S.A. during May 1949 was 5,486,062 grams according to *Pharm. J.*, **109**, 133 (1949).

For a review of the chemistry of streptomycin with an extensive bibliography, see "Recent Advances in Antibiotic Research," by P. Regna, *Chem. et Ind.*, **19**, 295 (1948); also *Science*, **102**, 40 (1945), and *Proc. Soc. Exp. Biol. and Med.*, **55**, 66 (1944).

**STRESS CORROSION CRACKING** — A type of failure encountered in a variety of ferrous and non-ferrous alloys, which are susceptible under some environments to selective corrosion along a more or less continuous path favourably oriented for high stress components to pull them asunder. Some plastics have also been reported as failing in this manner. (See *Symposium on Stress-Corrosion Cracking of Metals* (American Society for Testing Materials, Philadelphia); and *Corrosion*.)

**STROMEYERITE** — A mineral double sulphide of silver and copper ( $Ag_2S, Cu_2S$ ) found in Arizona and elsewhere.

**STRONTIANITE** — See Strontium.

**STRONTIUM (Sr) and its Compounds** — Atomic weight 87.63. See Elements for other data. Strontium is contained as carbonate ( $SrCO_3$ ) in the mineral known as *strontianite* (crystal system No. 4, and sp. gr. about 3.6); in *brewsterite* as a complex silicate, and in *celestite* as

sulphate ( $\text{SrSO}_4$ ). High-grade deposits of celestite are found in Mexico, Spain, and England and some impurer deposits in Canada and the United States. Celestite has found a wide use in the petroleum industry as a substitute for barite as a weighting agent in oil-well drilling fluid. This material is also employed in paints, sealing compounds for electric batteries, asphaltic compositions, rubber, and sealing wax. In these applications it is a substitute for barite and lithopone. Ground strontianite is used for desulphurizing and dephosphorizing steel, acting as a flux in the open-hearth furnace without damage to the furnace lining. The fluidity of the slag is increased with the addition of strontianite without losing its basic properties. (See *Mineral Resources* (U.S. Bureau of Mines), 1915, Pt. 2, 166, on "Barytes and Strontium" for map of the deposits and workings in the United States; and *Strategic Minerals*, by J. B. DeMille (McGraw-Hill Book Co., New York).)

The metal is soft, of a pale yellow colour, and has to be kept in naphtha, as it readily oxidizes in the air and possesses the property of decomposing water. It is prepared by the electrolysis of the fused chloride, and, like magnesium, it burns brilliantly upon ignition in the air, producing the monoxide ( $\text{SrO}$ ).

**Strontium Oxides** — The monoxide (strontia), like lime, combines with water, with evolution of heat, forming the hydroxide ( $\text{Sr}(\text{OH})_2$ ), which is strongly alkaline and more soluble in water than calcium hydroxide. It is used on a large scale in the purification of sugar.

The peroxide ( $\text{SrO}_2$ ) (formed by passing oxygen over the heated monoxide) parts with oxygen upon heating to redness, and is reduced to the monoxide. It is obtained in pearly crystals having the composition  $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$  by adding hydrogen peroxide to a solution of the hydroxide, and is used to some extent in bleaching; it loses its water when heated at  $100^\circ \text{C}$ .

**Strontium Chloride** ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ) is a white, crystalline salt, soluble in water and alcohol, and used in pyrotechny for the production of red flames.

**Strontium Nitrate** ( $\text{Sr}(\text{NO}_3)_2$ ), obtained by dissolving the oxide or carbonate in dilute nitric acid, is a white, crystalline salt used in the production of red lights and fireworks. It crystallizes with water as  $\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , and when heated with combustible matter, the mixture fires and burns with a characteristic crimson colour.

**Strontium Carbonate** ( $\text{SrCO}_3$ ) is white, practically insoluble in water, and used in the manufacture of pyrotechnics and iridescent glass.

**Strontium Sulphate** ( $\text{SrSO}_4$ ) is white, nearly insoluble in water, and finds increasing use as a paint pigment.

**Strontium Saccharate** (Saccharate Strontium) — See Sugar.

**Strontium Chlorate** ( $\text{Sr}(\text{ClO}_3)_2$ ) is a white, crystalline substance, soluble in water, and used in making red-fire, etc.

The bromide, iodide, and salicylate are used in medicine.

**STROPHANTHUS** — The dried ripe seeds of *Strophanthus Kombe* from which the awns or beards have been removed, obtained from tropical

East Africa. It contains from 7 to 10 per cent. of a mixture of glycosides, known as strophanthin-K and is used in medicine for the treatment of heart disease. (See *Digitalis and Other Cardiotonic Drugs*, by E. R. Movitt (Oxford Medical Publications, New York) ; *Digitalis*, and *Ouabain*.)

**STRYACIN** — See Balsams, and Cinnamic Alcohol.

**STRYCHNINE** ( $C_{21}H_{22}O_2N_2$ ) — A white, crystalline alkaloid, obtained from the seeds of *Strychnos Nux-vomica* and other species of *Strychnos* ; sparingly soluble in water ; soluble in alcohol and chloroform ; insoluble in ether ; m.p.  $270^\circ$  to  $280^\circ$  C., with decomposition. It occurs in combination with brucine, to which it is chemically related. Strychnine stimulates the spinal reflexes and is used in medicine, in small doses, as a constituent of bitter tonics. The chemistry of Strychnine is described by Thomas A. Henry in *The Plant Alkaloids* (J. and A. Churchill, London ; Blakiston, Philadelphia). (See *Nux Vomica*.)

**STUCCO** — See Calcium (Compounds).

**STYRENE** (Styrol, Cinnamene, Phenyl Ethylene) ( $C_6H_5CH : CH_2$ ) — A refractive, oily, yellowish liquid of aromatic odour, with a sp. gr. of 0.906 and b.p.  $145^\circ$  C., obtained from liquid storax (styrax), and used in medicine, perfumery, and synthetic rubber. It is soluble in alcohol and ether, and polymerizes spontaneously upon standing, into a jelly-like mass. Under controlled polymerization with butadiene, the product is synthetic rubber GR-S. (See Weiss, *Chem. Eng. News*, 26, 238 (1948) ; and Rubber.)

**STYRONE** — See Cinnamic Alcohol.

**SUB** — A chemical prefix used to indicate a lower valency ; also "less than normal" in respect of basic substances, such as lead suboxide ( $Pb_2O$ ) and the subacetate (basic) acetate of lead ( $Pb(C_2H_3O_2)_2 \cdot Pb(OH)_2$ ).

**SUBERIC ACID** ( $COOH(CH_2)_6COOH$ ) — A member of the oxalic series of acids, originally obtained by the action of nitric acid upon cork, but easily prepared, similarly, from oleic acid or other fatty acids. It is a crystalline body which melts at approximately  $142^\circ$  C., dissolves readily in boiling water, and mixes with fixed oils. When strongly heated, it gives off suffocating vapours.

**SUBLIMATION** — Sublimation (dry evaporation), particularly under reduced pressure, can be usefully employed for the purification of many substances, such as sulphur, iodine, naphthalene, camphor, benzoquinone, anthraquinone, cantharidin, and caffeine, from crude materials, etc. (See Heat.)

**"SUBOX"** — A paint consisting of a suspension of colloidal lead produced electrically. It may be applied when rubbed with linseed oil to iron and other metals, wood, cardboard, and cement ; a second coating producing a lustrous lead skin.

**SUBSTITUTION PRODUCTS** are those which result from the substitution of one element or radical by another in any chemical substance. For example, methane ( $\text{CH}_4$ ) yields four substitution products with chlorine by replacement of respectively 1, 2, 3, and 4 atoms of hydrogen, represented by  $\text{CH}_3\text{Cl}$  (methyl chloride),  $\text{CH}_2\text{Cl}_2$  (methylene chloride),  $\text{CHCl}_3$  (chloroform), and  $\text{CCl}_4$  (carbon tetrachloride). Again, nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ) is a substitution product obtained from benzene ( $\text{C}_6\text{H}_6$ ) by the replacement of 1 atom of hydrogen by the group  $\text{NO}_2$ . (See A. E. Remick's *Electronic Interpretations of Organic Chemistry* (John Wiley and Sons, New York); Radicals, and Valencies.)

**SUBSTRATE** — See Enzymes.

**SUCCINAMIDE** — See Amides.

**SUCCINIC ACID** ( $\text{COOH}(\text{CH}_2)_2\text{COOH}$ ) is a saturated dibasic acid of the oxalic acid series, and is found amongst the products of the distillation of amber and in certain animal juices, vegetables, and resins. It can be prepared in several ways, including the oxidation of butyric acid and the hydrolysis of ethylene dicyanide. It forms large colourless crystals, is soluble in water, fuses at  $190^\circ\text{C}$ ., and at  $235^\circ\text{C}$ . its vapour is dissociated into succinic anhydride ( $(\text{CH}_2\text{CO})_2\text{O}$ ) and water. Its alkaline salts are soluble in water.

**SUCCINIMIDE** — See Imides.

**SUCCINYLSULPHATHIAZOLE** (“Colistatin,” “Sulphasuxidine”) ( $\text{C}_{13}\text{H}_{13}\text{O}_5\text{N}_3\text{S}_2\cdot\text{H}_2\text{O}$ ) — A white or slightly off-white, odourless, tasteless, crystalline compound, namely, *p*-2'-sulphonthiazolylamidossuccinanilic acid,  $\text{HOOC}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{HN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}:\text{N}\cdot\text{CH}:\text{CH}\cdot\text{S}$ ,  
└──────────┘

prepared by condensation of sulphathiazole and succinic acid; almost insoluble in water; sparingly soluble in alcohol and acetone; insoluble in ether and chloroform; soluble in aqueous solutions of alkali hydroxides and carbonates; m.p.  $188^\circ$  to  $195^\circ\text{C}$ . with decomposition. It is practically unabsorbed on oral administration and is used for the treatment of local intestinal infections such as bacillary dysentery and ulcerative colitis. (See Sulphanilamide.)

“**SUCHAR**” — A vegetable carbon used for sugar refining, etc.

**SUCRASE** — See Invertase.

**SUCROSE** — See Sugar.

“**SUDERMO**” — See Mesulphen.

**SUGAR** (Cane Sugar, Beet Sugar, Saccharose, Sucrose) ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ) — Although the title sugar is a generic one, being given by chemists to a large range of aldehydic and ketonic bodies containing several alcoholic hydroxyls (see Fructose, Lactose, Dextrose, Maltose, and Arabinose), the word as used by the layman is meant to refer to the non-reducing disaccharide known as cane-sugar. Chemically it is 1-(D-fructofuranosido)-D-glucose, a dextro-rotatory, sweet-tasting substance, which on hydrolysis yields a mixture of equimolecular amounts of D(+)-glucose and D(−)-fructose, the resulting mixture being known as invert sugar, as it is lævo-rotatory.

The manufacture of cane sugar is an important industry in the West Indies, the Philippines, Queensland, Natal, and South-eastern United States, while the beet sugar industry is carried on in England, roots with a sugar content of 16.5 to 18.4 per cent. being produced at some fourteen factories (at Kelham, Cantley, Ely, Ipswich, and elsewhere), and in many parts of the United States. The area planted with sugar-cane in India is estimated at about two and a half million acres, and the beet sugar area in England in 1930 at about 380,000 acres. The average yield per acre of topped and washed sugar beet in Great Britain is 8.75 tons and the average sugar content 16.7 per cent.

Sugar is a hard, white, crystalline, sweet substance, occurring in the stems or juices of certain grasses and many plants, including the red-beet and sugar-maple, and particularly the sugar-cane (*Saccharum officinarum*) of many cultivated varieties, from which it is produced by pressure between rollers and subsequent purification, one ton of sugar-cane yielding about from 150 to 225 pounds of sugar. The sugar juice, containing from 83 to 88 per cent. water, as expressed from the canes, is first of all defecated, that is, treated with milk of lime to neutralize acidic ingredients, and boiled to coagulate the albuminous matters contained in the juice. The excess of lime is then carbonated by the passage of carbon dioxide or removed by precipitation with phosphoric acid. The resulting settled or filtered liquor is evaporated *in vacuo*, and yields a mixture of sugar crystals (monoclinic prisms) and syrup, the former being separated from the latter (treacle) by centrifugalization. It is refined by dissolving in water, filtration through kieselguhr, and decoloration by percolation through charcoal, after which it is again concentrated and crystallized. If animal charcoal be used nearly 100 per cent. on the net weight of sugar melted is stated to be required, whereas only 1 per cent. of good vegetable charcoal, such as "Suchar," or other good active carbon, is said to suffice.

#### SUGAR, WORLD PRODUCTION FOR THE YEAR 1939

Data arranged and rounded off by the Editor.

				Short Tons	
				Cane	Beet
U.S.A.	..	..	..	1,800,000	580,000
Cuba	..	..	..	3,030,000	
Puerto Rico	..	..	..	850,000	
Hawaii	..	..	..	960,000	
Philippines	..	..	..	980,000	
Java	..	..	..	1,710,000	
British India	..	..	..	3,800,000	
Europe	..	..	..	—	9,700,000
Sum of above	..	..	..	13,130,000	10,280,000
WORLD TOTAL				22 600 000	11 500 000

The molasses (treacle) containing some crystalline sugar still in solution is treated with a solution of strontium hydroxide, which forms a sparingly soluble combination with it (strontium saccharate,  $C_{12}H_{22}O_{11} \cdot 2SrO$ ), and after removal by the "Oliver" or other filter, is decomposed while suspended in water, by the action of carbon dioxide, thus forming insoluble strontium carbonate, the sugar meanwhile passing into solution, from which it is recovered by concentration and crystallization. A process has been devised by the Great Western Sugar Refining Co., Colorado, whereby barium hydroxide can be used in place of strontium hydroxide with certain advantages, and there is a method for converting the resulting barium carbonate into hydroxide, using an electric furnace for effecting part of that purpose.

The molasses finally left is used for making rum, or ordinary alcohol, and the "bagasse" ("bégasse"), or crushed sugar-cane mass, is either subjected to a diffusion process to extract some further proportion of its sugar content or used as fuel. Bagasse may be regarded as a mixture of alpha-cellulose, pentosans, and lignin. It is also utilized for the manufacture of an artificial building material: after being "chipped," "cooked," and washed, it is sent as pulp to the "beaters," where it is worked until the fibres are of the proper length, after which it is dried and marketed as "Celotex," which can be worked like timber, and, although lighter than wood, is said to be quite solid and homogeneous.

In course of the evaporation of maple sap (from *Acer saccharinum* of N. America and other species) to the syrup stage, a precipitate called "sand," containing from 60 to 83 per cent. of calcium malate, is deposited, and finds use in the preparation of baking-powders, etc.

Beets, after washing, are cut up by slicers into cossettes and the sugar extracted by hot water, the juice being then subjected to "carbonation" by treating it hot with about 2 per cent. of lime and a current of carbon dioxide. After separating from the calcium carbonate, the syrup is evaporated, and finally boiled in a steam-heated jacketed pan until it becomes a mass of crystals in a syrupy mother-liquor. This so-called "massecuite" is then centrifugalized to separate the crystals from the mother-liquor.

In a modified process ("De Vecchis") of making beet sugar the beet slices are desiccated at 90° to 110° C., thus coagulating the albuminoids and breaking the cells. These dried slices can be kept for a long time, and by washing with hot water yield a comparatively pure juice which is purified by lime powder, the excess of which is precipitated as phosphate, the liquid being subsequently filtered, crystallized, and the product centrifugalized as usual. This process permits the sugar-making to be carried on at any time during the year. The residue constitutes a nutritious feeding-stuff for cattle. (See J. Kwantes on "Chemistry in Beet-Sugar Manufacture" (*Chem. and Ind.*, 50, 306 (1931)).)

Mangolds contain from 6.6 to 12.4 per cent. sugar calculated on the dry material, turnips from 10.1 to 14.0 per cent., and carrots from 7.5 to 11.2 per cent. Sugars are also present in Jerusalem artichokes.

Various palms growing in tropical regions, particularly in the Philippine Islands, yield a syrupy sap containing about 15 per cent. sugar, and are employed by natives for making sugar and "toddy," while the banana contains in the ripe state as much as 20 per cent. sugar.

The carob, which grows in Sicily and other parts of the Mediterranean countries, gives a fruit containing from 10 to 34 per cent. saccharose and from 8 to 30 per cent. of reducing sugars. The sugars can be extracted by methyl alcohol.

It is reported that synthetic sugars of the hexose group have been produced by the action of light upon carbon dioxide in presence of water, using a catalyst of nickel or cobalt carbonate. (See Carbohydrates, and Photo-catalysis.)

Sugar melts at 160° C. into what is known as barley-sugar, and when further heated to from 170° to 180° C. decomposition occurs, with darkening, loss of water, and formation of so-called "caramel." When subjected to the action of acids, cane sugar is "inverted" by hydrolysis, and whereas it is dextro-rotatory, the invert sugar which is formed is lævo-rotatory and consists of an equal molecular mixture of fructose and glucose (lævulose and dextrose).

The relative sweetness of various sugars, as determined by the "minimum concentration" method, is given as follows: Cane sugar as 100, lævulose 173.3, dextrose 74.3, maltose 32.5, and lactose 16.0.

There is a patented process for obtaining glutamic acid from "schlempe," a by-product of beet molasses (probably bégasse).

The production of sugars (chiefly glucose) from wood and sawdust is referred to under the headings of Glucose, and Wood, and that of "corn" sugar under heading of Dextrose.

Sugar in its several forms is a valuable food, and is largely used as a sweetener, in the preparation of syrups, preserves, and jams, and molasses is used for the manufacture of alcohol, etc. It is marketed in many forms, such as "loaf," "cube," "lump," "granular," "icing," etc. The so-called "soft" sugars contain a proportion of molasses, also of invert sugar.

*References:* "The World's Sugar Industry," by Lewis Eynon (Lecture, Institute of Chemistry); "Industrial Uses of Cane Sugar," by G. J. Cox and M. L. Dodds (*Ind. Eng. Chem.*, **25**, 967 (1933)); *The Constitution of Sugars*, by W. N. Haworth (E. Arnold and Co., London); *A Handbook for Cane-Sugar Manufacturers and their Chemists*, by G. L. Spencer (Chapman and Hall, Ltd., London); *Cane Sugar: A Textbook on the Agriculture of the Sugar Cane, the Manufacture of Cane Sugar, and the Analysis of Sugar House Products*, by N. Deerr; *Cane Sugar and Its Manufacture*, by H. C. P. Geerligs; *The Sugar Beet in America*, by F. S. Harris; *Sugar: Its Production, Technology and Uses*, by Andrew Van Hook (The Ronald Press, New York); Caramel, Carbohydrates, Fermentations, Glucose, Malt, Sorghum, Ventzke Degrees, Waxes (Sugar-Cane), and Yeasts.

**SUGAR-CANE WAX** — See Waxes.

**SUGAR OF LEAD** — See Lead (Acetate).

**SUGAR OF MILK** — See Lactose.

**SUGAR-SOAP** — An alkaline, readily soluble soap preparation used by painters for washing down before applying fresh coats of paint or varnish.

**SUINT** — See Wool.

**"SULAMYD"** — See Sulphacetamide.

**SULPHACETAMIDE** ("Albucid," "Steramide," "Sulamyd") ( $C_8H_{10}O_3N_2S$ ) — A white or slightly off-white, crystalline compound, namely, *p*-aminobenzenesulphonacetamide, ( $H_2N.C_6H_4.SO_2.NH.CO.CH_3$ ), prepared by acetylation of sulphanilamide; slightly soluble in water; insoluble in ether and chloroform; soluble in acetone, mineral acids, and solutions of alkali hydroxides; m.p.  $181^\circ$  to  $184^\circ$  C. It is used in medicine for the treatment of bacterial infections, particularly of the urinary tract.

**Sulphacetamide Sodium** — The sodium derivative of sulphacetamide having the molecular formula  $C_8H_9O_3N_2SNa.H_2O$ ; very soluble in water. A 30 per cent. solution is used in medicine as eye drops for the treatment of ophthalmia neonatorum and other infections of the eye. (See Sulphanilamide.)

**SULPHADIAZINE** ( $C_{10}H_{10}O_2N_4S$ ) — A white, odourless, tasteless compound, namely, 2-(*p*-aminobenzenesulphonamido)-pyrimidine,  $H_2N.C_6H_4.SO_2.NH.C:N.CH:CH.CH:N$ , prepared by interaction be-

tween *p*-acetamidobenzenesulphonyl chloride and 2-aminopyrimidine and deacetylation by boiling with aqueous sodium hydroxide solution; very sparingly soluble in water; sparingly soluble in alcohol; soluble in mineral acids and in aqueous solutions of alkali hydroxides; m.p.  $252^\circ$  to  $256^\circ$  C. It is used in medicine for the treatment of bacterial infections and is one of the least toxic of the sulphonamides.

**Sulphadiazine Sodium** — The sodium derivative of sulphadiazine having the molecular formula  $C_{10}H_9O_2N_4SNa$ ; very soluble in water. A sterile aqueous solution is used for intravenous administration when oral administration of sulphadiazine is not possible. (See Sulphanilamide.)

**SULPHADIMIDINE** (Sulphadimethylpyrimidine, "Sulphamethazine," "Sulphamezathine") ( $C_{12}H_{14}O_2N_4S$ ) — A white, odourless, tasteless crystalline powder, namely, 2-(*p*-aminobenzenesulphonamido)-4,6-dimethylpyrimidine; prepared by condensing *p*-acetylaminobenzene-sulphonyl chloride with 2-amino-4,6-dimethylpyrimidine and subsequent deacetylation; sparingly soluble in water and alcohol; insoluble in ether and chloroform; soluble in solutions of alkali hydroxides; m.p.  $196^\circ$  to  $199^\circ$  C. It is well absorbed on oral administration and is one of the least toxic and most active of the sulphonamides.

**Sulphadimidine Sodium** — The sodium derivative of sulphadimidine; very soluble in water. A sterile solution is used for the intravenous administration of sulphadimidine. (See Sulphanilamide.)

**SULPHAGUANIDINE** ( $C_7H_{10}O_2N_4S \cdot H_2O$ ) — A white, odourless, tasteless, crystalline compound, namely, *p*-aminobenzenesulphonylguanidine monohydrate, prepared by fusing dicyandiamide with *p*-aminobenzenesulphonamide; sparingly soluble in water, alcohol, and acetone; insoluble in ether and chloroform; m.p. (when anhydrous)  $190^\circ$  to  $192.5^\circ C$ . It is poorly absorbed on oral administration and is used for the treatment of infections of the intestinal tract such as bacillary dysentery and ulcerative colitis. (See Sulphanilamide.)

**SULPHAMATE LEAD SALTS** (Du Pont) — Used for lead plating to produce a relatively pore-free lead deposit.

**"SULPHAMERAZINE"** ( $C_{11}H_{12}O_2N_4S$ ) — A white, odourless, tasteless, crystalline powder, namely, 2-(*p*-aminobenzenesulphonamido)-4-methylpyrimidine,  $H_2N \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot C : N \cdot C(CH_3) : CH \cdot CH : N$ , pre-

pared by condensing *p*-acetylaminobenzenesulphonyl chloride with 2-amino-4-methylpyrimidine and subsequent deacetylation; sparingly soluble in water, alcohol, and acetone; insoluble in ether and chloroform; soluble in solutions of alkali hydroxides; m.p.  $235^\circ$  to  $236^\circ C$ . It is one of the least toxic and most active of the sulphonamides and is stated to be therapeutically effective in a half the dosage of sulphadiazine or sulphadimidine. (See Sulphanilamide.)

**"SULPHAMETHAZINE"** — See Sulphadimidine.

**"SULPHAMEZATHINE"** — See Sulphadimidine.

**SULPHAMIC ACID** (Du Pont) ( $HO \cdot SO_2 \cdot NH_2$ ) — A white crystalline solid, odourless and non-volatile, non-hygroscopic, and moderately soluble in water. Used as a sulphonating and sulphating agent for primary alcohols, phenols, and unsaturated compounds; with aldehydes yields methylol derivatives. The calcium, barium, and lead salts are very soluble in water.

**SULPHANILAMIDE** ("Ambesid," "Colsulanyde," "P.A.B.S.," "Prontosil Album," "Streptocide," "Sulphonamide P") ( $C_6H_8O_2N_2S$ ) — A white, odourless, crystalline compound, namely, *p*-aminobenzenesulphonamide ( $C_6H_4(NH_2)$  (I) ( $SO_2NH_2$ ) (4)), slightly soluble in water; sparingly soluble in alcohol; insoluble in ether, chloroform, and benzene; m.p.  $164.5^\circ$  to  $166.5^\circ C$ .

Sulphanilamide is the simplest member of the sulphonamides, a series of compounds used in medicine for the treatment of bacterial infections. The introduction of these compounds dates from the original discovery by Domagk in 1935 that the dyestuff Prontosil Rubrum possessed streptocidal properties on administration to experimentally infected animals. This led to the use of Prontosil for the treatment of hæmolytic streptococcal infections. It was subsequently shown by Trefouel and his co-workers that the therapeutic activity of Prontosil is due to a simpler compound, sulphanilamide, which is formed by the breakdown of Prontosil in the body. Sulphanilamide was thus introduced to replace Prontosil for the treatment of streptococcal infections. A notable advance in the study of the compounds

was made by Ewins and his colleagues, who found that substitution of one of the hydrogen atoms in the sulphonamido group by pyridine produced a compound ("M and B 693") possessing activity against a wider range of organisms. This compound, which subsequently became known as sulphapyridine, was successfully introduced for the treatment of pneumococcal pneumonia and also proved of value in the treatment of infections due to gonococci and the organisms of gas-gangrene. Sulphapyridine suffered from a number of disadvantages owing to its toxic side-effects and later work has been directed towards the production of compounds having comparable therapeutic effect but lower toxicity. These include sulphathiazole, sulphadiazine, sulphacetamide, sulphadimidine, and sulphamerazine.

Another group of derivatives of sulphanilamide consists of compounds of low solubility which are poorly absorbed on oral administration. This group, which includes sulphaguanidine, phthalylsulphathiazole, and succinylsulphathiazole, is used for the treatment of intestinal infections such as bacillary dysentery and ulcerative colitis.

The mode of action of the sulphonamides has been the subject of much investigation. The action on susceptible organisms is bacteriostatic rather than bactericidal and the therapeutic effect of these compounds is due to inhibition of the growth of the infecting organisms, thus enabling the normal defence mechanisms of the body to deal with the infection. The action of the sulphonamides can be antagonized by small concentrations of *para*-aminobenzoic acid and the theory has been advanced that the sulphonamides act by taking the place of *para*-aminobenzoic acid in an enzyme system which is essential for the normal growth of the organisms.

See *The Sulfonamides and Allied Compounds*, by E. H. Northey (Reinhold Publishing Corp., New York); *The Medical Use of the Sulphonamides*, M.R.C. War Memorandum No. 10, 1945 (H.M. Stationery Office, London); *Sulfanilamide Therapy of Bacterial Infections*, by R. R. Mellon *et al.* (C. C. Thomas, Springfield, Illinois); and "The Economic Impact of the Sulfonamides on the Drug Industry," by J. S. Zinsser (*Chem. and Eng. News*, **21**, 1159 (1943)).

**SULPHANILIC ACID** ( $C_6H_4(NH_2)(SO_3H)$  (1, 4)) — An intermediate for the preparation of dyestuffs and the sulphanilamide group of drugs. Made by interaction of aniline and sulphuric acid. Decomposes at 288° C.

**SULPHAPYRIDINE** — See Sulphanilamide.

**SULPHARSPHENAMINE** — See Arsphenamine.

"**SULPHASUXIDINE**" — See Succinylsulphathiazole.

**SULPHATES** — See Sulphur (Sulphuric acid), and individual metals; Dimethyl Sulphate, and Diethyl Sulphate.

"**SULPHATHALIDINE**" — See Phthalylsulphathiazole.

**SULPHATHIAZOLE** ("M and B 760," "Cibazole," "Thiazamide") ( $C_9H_9O_2N_3S_2$ ) — A white or slightly off-white, odourless, tasteless, crystalline compound, namely, 2-(*p*-aminobenzenesulphonamido)-thiazole,  $H_2N.C_6H_4.SO_2.NH.C:N.CH:CH.S$ , prepared by condensing

2-aminothiazole with *p*-acetamidobenzenesulphonyl chloride and subsequent deacetylation; sparingly soluble in water; slightly soluble in alcohol; soluble in dilute mineral acids and solutions of alkali hydroxides; m.p. 200° to 203° C. It is one of the most active of the sulphonamides, but is more toxic than sulphadiazine and sulphadimidine.

**Sulphathiazole Sodium** — The sodium derivative of sulphathiazole having the molecular formula  $C_9H_8O_2N_3S_2Na.5H_2O$ ; very soluble in water. A sterile solution is used for the intravenous administration of sulphathiazole. (See Sulphanilamide.)

**"SULPHETRONE"** — An organic compound, namely, 4,4'-bis(*γ*-phenyl-*n*-propylamino)-diphenylsulphone-tetrasodium sulphonate; an amorphous material, very soluble in water; insoluble in alcohol, chloroform, and ether. It is used, in conjunction with streptomycin or alone, for the treatment of tuberculosis. It has also shown promise in the treatment of leprosy. An account of the pharmacology of "Sulphetrone" is given by G. Brownlee, A. F. Green and M. Woodbine, *Brit. J. Pharmacol.*, **3**, 15 (1948). The treatment of experimental tuberculosis is described by G. Brownlee and C. R. Kennedy, *Brit. J. Pharmacol.*, **3**, 29 (1948). (See D. G. Madigan, *Lancet*, **255**, 174 (1948); M. G. Clay and A. C. Clay, *Lancet*, **255**, 180 (1948); Diasone, "Promin," and "Promizole.")

**SULPHIDES (Inorganic)** — See Sulphur (Compounds).

**SULPHIDES (Organic)** — The organic substances of the formula  $R-SH$  are known as thioalcohols or mercaptans, as they react with mercury, and are evil-smelling liquids of great use in the manufacture of hypnotics of the sulphonal class. Those of the formula  $R-S-R'$  are known as dialkylsulphides or thioethers, and those of the types  $R-S-S-R$  as disulphides, which are of great importance in biochemistry owing to their reversible reduction to thioalcohols in the presence of hydrogen donors, and their reformation from the mercaptans in the presence of hydrogen acceptors. The oxidation-reduction system thereby formed is of common occurrence in the living body, and plays an important part in modern theories of drug action. (See *The Basis of Chemotherapy*, by T. S. Work and E. Work (Gurney and Jackson, London).)

**SULPHINIC ACIDS** — Aliphatic or aromatic compounds containing the univalent grouping  $-SO.OH$  attached directly to a carbon atom. Alkyl sulphinic acids ( $C_nH_{2n+1}.SOOH$ ) are formed (along with mercaptans ( $C_nH_{2n+1}.SH$ )) by the reduction of alkyl sulphonyl chlorides ( $C_nH_{2n+1}.SO_2Cl$ ); and aryl, e.g.,  $C_6H_5.SOOH$ , by the reduction of aryl sulphonyl chlorides, e.g.,  $C_6H_5.SO_2Cl$ , with zinc dust and water, or by the reaction of benzene and sulphur dioxide in the presence of anhydrous aluminium chloride.

Alkyl sulphonic acids are readily soluble in water, hygroscopic, highly ionized, and their salts crystallize well. Aryl sulphonic acids are only slightly soluble in cold water, and they crystallize well.

**SULPHION** — This term is sometimes used to indicate the bivalent ion  $S^{2-}$  as derived from hydrogen sulphide, and at others to indicate the  $SO_4^{2-}$  radical or ion of a solution of metallic sulphate.

**SULPHITE LIQUOR AND PULP** — See Paper.

**SULPHITES** — See Sulphur (Compounds), and individual metals.

**SULPHOCARBOLATES** are salts of phenolsulphonic acid. The zinc salt has been used in medicine.

**SULPHOCYANIC ACID**, otherwise known as thiocyanic acid ( $HCNS$ ), is the sulphur analogue of cyanic acid ( $HCNO$ ).

**SULPHOCYANIDES (Sulphocyanates)** — See Thiocyanates.

**SULPHONAL (Sulphone Methane ; Acetone Diethyl Sulphone)**  $((CH_3)_2C(SO_2.C_2H_5)_2)$  — A colourless crystalline substance, prepared from acetone and mercaptan by action of hydrochloric acid, and used as a soporific and hypnotic. It melts at  $127^\circ C$ . and is soluble in alcohol.

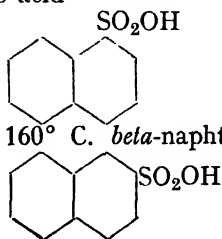
**"SULPHONAMIDE P"** — See Sulphanilamide.

**SULPHONATED OILS** — A number of these products are made and used commercially, "Turkey-red oil" being made as described under that heading by the action of strong sulphuric acid on castor oil. Other oils used include arachis, cotton-seed, cod and other fish oils, maize (corn) and neatsfoot oils. Commercial sulphonated castor oil varies in density from 1.022 to 1.025, and is miscible with water.

These oils, of which there are various types suitable for many applications, are used in branches of the leather trade to give softness and pliability to the articles ; also in the preparation of cotton fibre ; impregnating the warp threads of artificial silk ; for greasing wool, etc. ; as mordants for certain dyes ; as finishing oils for cotton, silk, linen, and leather ; also in paint and varnish-making. (See Soderdahl, *Soap, Perfumery and Cosmetics*, 21, 46 (1948) ; and Turkey-red Oils.)

**SULPHONATION** — Treatment of organic compounds with sulphuric acid, whereby sulphonic acids are produced, the products containing the group  $-SO_2OH$ . Thus benzene ( $C_6H_6$ ), treated with fuming sulphuric acids, yields benzene sulphonic acid ( $C_6H_5SO_2OH$ ) :  $C_6H_6 + H_2SO_4 = C_6H_5SO_2OH + H_2O$ .

When naphthalene is subjected to sulphonation, the position taken by the  $-SO_2OH$  group is dependent upon temperature. At  $80^\circ C$ . *alpha*-naphthalene sulphonic acid



predominates, whereas at  $160^\circ C$ . *beta*-naphthalene sulphonic acid

predominates and of course the latter reaction is much more rapid than the former on account of the higher temperature. Four naphthalene disulphonic acids are well known, namely, 2,6- and 2,7- at 200° C. and 1,5- and 1,6- by the action of chlorosulphonic acid ( $\text{Cl.SO}_2\text{OH}$ ) in the cold on naphthalene and on the *beta* acid respectively.

Sulphonation can be carried out not only by the use of liquid acid, but also in the vapour phase with, it is stated, a saving of acid. (See "Quantitative Control of Sulfonation Processes," by W. A. Simpson and J. C. Olsen (*Ind. Eng. Chem.*, **29**, 1350 (1937)); *Unit Processes in Organic Chemistry*, by P. H. Groggins (McGraw-Hill Book Co., New York); Naphthalenesulphonic Acid, and Sulphonated Oils.)

**SULPHONES** — Compounds of the formula  $\text{R}_2\text{SO}_2$ , being oxidation products of the thioethers,  $\text{R}_2\text{S}$ . Apart from the obsolescent hypnotics, such as sulphonal and trional, many compounds, such as derivatives of diaminodiphenylsulphone, have been tested as tuberculostatic agents. Diphenyl sulphone,  $(\text{C}_6\text{H}_5)_2\text{SO}_2$ , is a white solid, of m.p. 128° C. and b.p. 379° C.

**SULPHONIC ACIDS** — Aliphatic or aromatic compounds containing the univalent grouping  $-\text{SO}_2\text{OH}$  attached directly to a carbon atom. They are all strong acids, soluble in water, and forming salts, esters, amides, etc., just like the carboxylic acids, but differing from the latter in their high dissociation constants. Their salts are all water-soluble, and the addition of the  $-\text{SO}_2\text{OH}$  group to an otherwise insoluble compound is largely used, especially in the dye industry, to obtain a water-soluble product. There is enough difference in the solubilities of the *alpha* and *beta* naphthalene sulphonates of calcium and barium to make possible their separation by fractional crystallization—the *alpha* being the more soluble of the two.

The sulphonic acid group is easily replaced by the action of hot alkalis, resulting in the corresponding phenols. (See Sulphonation.)

**SULPHUR (S) (Brimstone) and its Compounds** — Atomic weight, 32.066 (1947). See Elements for other data; and also accompanying Chart. Large quantities of sulphur are found naturally in Japan, Spain, and the United States, also in volcanic districts, including Italy, Sicily, Chile, and Iceland, and there are considerable beds of it in the Løkken mines south-east of Trondheim (in Scandinavia), and in Transylvania, China, India, Texas, and Louisiana.

The Sicilian method of extraction is by a process in which the sulphur rock is ignited, the heat thus generated being used to melt the surrounding parts, attended with an approximate loss of 15 per cent. of the total sulphur.

In Louisiana and Texas, the comparatively pure sulphur is first of all melted underground by superheated water pumped into the deposit, and then forced up in the liquid state. This process is described in *Ind. Eng. Chem.*, **30**, (1938) by D. B. Mason (p. 740) on "The Sulfur Industry. History and Development," and by C. E. Butterworth and J. W. Schwab (p. 746) on "Sulfur Mining as a Processing Industry."

## SULPHUR-CONTAINING SUBSTANCES

## CHART SHOWING PRINCIPAL INTER-RELATIONSHIPS

Arrangement based on Valency and Reduction-Oxidation Properties  
Arranged by the Editor.

Hydrogen Sulphide $H_2S$	Sulphur $S$			Sulphurous Acid $H_2SO_3$	Sulphuric Acid $H_2SO_4$
				Sulphur Dioxide $SO_2$	Sulphur Trioxide $SO_3$
Sulphides		Thiosulphates $Na_2S_2O_3$	Hydrosulphites $Na_2S_2O_4$	Sulphites INORGANIC	Sulphates
INORGANIC				Soluble	INORGANIC
$Na_2S$ ; $NaHS$				$Na_2SO_3$	Soluble
Reactive with water				$NaHSO_3$	$Na_2SO_4$
$Al_2S_3$					$NaHSO_4$
Insoluble				Insoluble	Insoluble
$PbS$				$PbSO_3$	$PbSO_4$
ORGANIC	ORGANIC			ORGANIC	ORGANIC
Thioethers	Disulphides			Sulphinyl-Comp.	Sulphonyl-Comp.
$(C_6H_5)_2S$	$C_6H_5S.SC_6H_5$			Sulphoxides $(C_6H_5)_2SO$	Sulphones $(C_6H_5)_2SO_2$
$(ClCH_2CH_2)_2S$				Sulphinic Acids $C_6H_5.SO_2OH$	Sulphonic Acids $C_6H_5.SO_3OH$
Thioalcohols					
$C_6H_5.SH$				Sulphites $(CH_3O)_2SO$	Sulphates $(CH_3O)_2SO_2$
Thiophenols					
$C_6H_5.SH$					
Thiophene					
$CH:CH.CH:CH.S$					
Carbon disulphide $CS_2$	Soluble:	Pentathionates $BaS_5O_6$	Tetrathionates $BaS_4O_6$	Trithionates $BaS_3O_6$	Dithionates $BaS_2O_6$
		Thiolic Acids $R-\begin{smallmatrix} \diagup O \\ \diagdown SH \end{smallmatrix}$	Thionic Acids $R-\begin{smallmatrix} \diagup S \\ \diagdown OH \end{smallmatrix}$	Thion-Thiolic Acids $R-\begin{smallmatrix} \diagup S \\ \diagdown SH \end{smallmatrix}$	
		Thiocarbonic Acids			
		Mono $\begin{smallmatrix} RO \\ RO \end{smallmatrix} > C = S$			
		Di $\begin{smallmatrix} RO \\ RS \end{smallmatrix} > C = S$			
		Tri $\begin{smallmatrix} RS \\ RS \end{smallmatrix} > C = S$			
		$K_2CS_3$			

Sulphur is also found naturally in various combinations as sulphides, of which the best known are *galena*, or lead sulphide ( $PbS$ ); *zinc blende*, or zinc sulphide ( $ZnS$ ); *iron pyrite*, or iron sulphide ( $FeS_2$ ); *copper pyrite* ( $Cu_2Fe_2S_4$ ), and *cinnabar*, or mercury sulphide ( $HgS$ ). (See Pyrites.)

The mineral *gypsum*, or calcium sulphate ( $CaSO_4.2H_2O$ ), contains sulphur in combination with calcium and oxygen and water; whilst *heavy spar* also contains sulphur in the form of barium sulphate ( $BaSO_4$ ).

Sulphur, as obtained from its crude natural form, is purified by melting and vaporization (sublimation). As a constituent of iron pyrite, it is utilized in the manufacture of sulphuric acid, and it can be recovered from the sulphurized oxide of iron (spent oxide) resulting from the process used in gasworks for freeing the gas from hydrogen sulphide. This is done either by burning off the sulphur into the form

of sulphur dioxide or oxidation of the sulphurized mass, thereby revivifying the ferric oxide:  $4\text{FeS} + 3\text{O}_2 = 2\text{Fe}_2\text{O}_3 + 4\text{S}$ , the sulphur thus set free being subsequently distilled or burnt off. (See below on Sulphur Recovery.)

### PYRITES, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country	Pyrites Sulphur Content Millions of Metric Tons				
Spain .. .. .	..	..	..	1.1	
Norway .. .. .	..	..	..	0.4	
Italy .. .. .	..	..	..	0.4	
Portugal .. .. .	..	..	..	0.3	
Germany .. .. .	..	..	..	0.2	
Greece .. .. .	..	..	..	0.1	
Sweden .. .. .	..	..	..	0.1	
				<hr/>	2.6
U.S.S.R. .. .. .	..	..	..		0.6*
U.S.A. .. .. .	..	..	..	0.2	
Canada .. .. .	..	..	..	0.1	
				<hr/>	0.3
Cyprus .. .. .	..	..	..		0.2
					<hr/>
Sum of above .. .. .	..	..	..		3.7
WORLD PRODUCTION .. .. .	..	..	..		4.0*

\* Estimated.

### SULPHUR, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country					Sulphur Metric Tons
Italy .. .. .	..	..	..	..	340,000
U.S.A. .. .. .	..	..	..	..	2,700,000
Chile .. .. .	..	..	..	..	20,000
Japan .. .. .	..	..	..	200,000*	
Netherlands Indies .. .. .	..	..	..	20,000	
				<hr/>	220,000
Sum of above .. .. .	..	..	..		3,280,000

WORLD PRODUCTION, approximately the above.

\* Estimated.

Sulphur was also probably produced in Bolivia, China, Cuba, Egypt, Mexico, Palestine, Peru, Spain, Taiwan, U.S.S.R. in minor amounts.

**SULPHUR PRODUCTION IN SICILY AND THE UNITED STATES BY YEARS**  
 Data arranged and rounded off by the Editor.

Year	Sicily Metric Tons	Year	United States Long Tons
1907-08, 1 year	428,000	1909-13, 5-year aver.	401,000
1910-11, 1 year	392,000	1914-16, 3-year aver.	530,000
1916-17, 1 year	184,000	1917-20, 4-year aver.	1,235,000
1921-22, 1 year	187,000	1921-22, 2-year aver.	1,855,000
1937-39, 3-year aver.	340,000	1937-39, 3-year aver.	2,700,000
	Long Tons		
1924	290,000	1924	1,221,000
1926	267,000	1926	1,890,000
1928	291,000	1928	1,982,000
1930	345,000	1930	2,589,000
1932	370,000	1932	890,000
1934	359,000	1934	1,421,000
1936	343,000	1936	2,016,000
1938	374,000	1938	2,393,000
1940	325,000	1940	2,732,000
1942	223,000	1942	3,461,000
1944	37,000	1944	3,218,000*

\*Of this amount Texas 2,582,000 ; Louisiana 636,000

Sulphur affords one of the most interesting instances of substances which can assume a number of varying or so-called allotropic forms. In its ordinary form, it is a yellow crystalline body of rhombohedral formation, but by melting it under certain conditions it can be obtained in the form of monoclinic needles of transparent character which melt at  $119.2^{\circ}\text{C}.$ , are of sp. gr. 1.96, and upon exposure to the air gradually lose their transparency, crumble up, and assume once more the rhombohedral form. The ordinary rhombic form has a density of 2.07, and melts at about  $112.8^{\circ}\text{C}.$  to a yellow, limpid liquid. If the temperature be allowed to rise to  $180^{\circ}\text{C}.$ , sulphur becomes quite viscid and darkens very much in colour. If the heat be still further raised to  $260^{\circ}\text{C}.$ , it becomes less viscid, but not so fluid as when first melted. If, when in the viscous state, it be allowed to cool suddenly (as by

pouring it into cold water), it solidifies into a soft mass, which can be drawn out into elastic threads, having a sp. gr. of 2.05, and is not soluble in carbon disulphide, whereas the natural crystalline form has a sp. gr. of 2.07 and is very soluble. This form can be again transformed into the original by heating it to 100° C., when it suddenly returns to the brittle condition with an evolution of heat ; a change which also takes place if it is kept for a short time. Precipitated sulphur is rapidly and completely soluble in carbon disulphide and also slowly so in methylated spirit and petroleum spirit, whereas the sublimed substance is only soluble to about 83 per cent. in each of these solvents

When melted sulphur is cooled until a solid crust covers the surface and the remaining liquid content poured off, the sides of the vessel will be found covered with long, needle-shaped (monoclinic) crystals, as previously mentioned.

Crystals deposited from a solution of sulphur in carbon disulphide are of the rhombic character, while those deposited from alcohol and chloroform are of the monoclinic description.

It is stated that sulphur can be activated by the silent electric discharge, and in this form shows an increased activity towards hydrogen and carbon monoxide (Schwarz and Schenk).

Sulphur may be sublimed, that is to say, it can be vapourized by heat, and the vapour can then be condensed at a temperature below its melting-point into the solid state, so-called "flowers of sulphur," consisting of minute crystals.

The boiling-point of sulphur is 444.6° C.

In precipitated form, as obtained, for example, from polysulphides in solution, it is known as "lac sulphur" and this form is used by agriculturists for depositing on plants after spraying them with lime-sulphur solution, for fungicidal application.

Sulphur is marketed in the forms of crystals, "roll," "precipitated," and "sublimed" (flowers).

Sulphur exercises a valuable toxic action as a fungicide ; for example, flowers of sulphur applied in paste form to hot-water pipes in green-houses will keep in check diseases of the mildew type on plants kept in the houses, its activity being largely dependent upon its fineness of division. Sublimed powdered sulphur is largely used in Italy, France, and elsewhere, as a fungicide for treating grape-vines.

Sulphur is used in the manufacture of gunpowder and sulphuric acid, also in the preparation of sulphite cooking liquor for making wood-pulp for paper, in the preparation of ultramarine, in the vulcanization of rubber, in pharmacy (in compounding so-called milk of sulphur and other medicaments), as a fertilizer, and for fumigating beer casks and infected rooms.

A slight sulphur dusting is alleged to obviate the spontaneous inflammation of oily wiping rags and other materials. It is also used in admixture with other substances for the production of almost non-inflammable moulded objects of high plasticity. For example, a mixture of 60 parts sand and 40 parts sulphur forms a good substitute for

cement, and can be used for setting bricks in acid towers or in the construction of acid-proof tanks, the tensile strength being almost 400 pounds per square inch. Concrete articles dipped in molten sulphur will take up from 14 to 16 pounds per cubic foot, and the normal strength is stated to be thus increased ten-fold. Dense sandstone will take up some 84 per cent. of its own volume when similarly treated, and wood can be usefully preserved by sulphur impregnation. Large proportions of sulphur can also be used in conjunction with pitch or bitumen as good binding agents in construction.

Sulphur plays a more important part in chemical industry than any other element. Since about 1910 the United States has dominated the sulphur industry as is shown by the table of production in Sicily and the United States. In 1941-45 the distribution of sulphur consumption in the United States was as follows :

Heavy chemicals	..	..	..	52 per cent.
Fertilizers and insecticides	..	..	..	20 "
Pulp and paper	..	..	..	12 "
Explosives	..	..	..	3 "
Paints and varnish	..	..	..	3 "
Dyes and coal-tar products	..	..	..	3 "
Rubber	..	..	..	2 "
Sum of above	..	..	..	95 "
Other industries	..	..	..	5 "

**Sulphur Oxides** — Sulphur burns in the air with a blue flame and gives rise to the production of sulphur dioxide ( $\text{SO}_2$ ), a gas of pungent, irritating nature which may be condensed and liquefied, or a solution of it in water can be prepared. The liquefied gas is used to some extent as a refrigerating agent, also in preservation of foodstuffs and preparation of dyes. In all three forms it is used for disinfecting purposes and for bleaching straw, silk, wool, and sponge. (See Fumigation.)

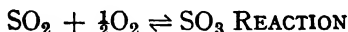
As employed for use in the manufacture of sulphuric acid, the gas is produced using burners of various types for combustion of the sulphur or the roasting of pyrites. Among these may be mentioned the "Wedge Sulphur Furnace," and the "Glensfalls Rotary Sulphur Burner".

Of the oxides of sulphur, the two most important are the gaseous dioxide ( $\text{SO}_2$ ) (which boils at  $-10.0^\circ \text{C}$ . under atmospheric pressure, and is soluble in water to the extent of 79.8 volumes in 1 volume at  $0^\circ \text{C}$ .), and the trioxide ( $\text{SO}_3$ ). Below  $7^\circ \text{C}$ . a saturated solution of sulphur dioxide is stated to be supersaturated with respect to the crystalline hydrate  $\text{SO}_2 \cdot 7\text{H}_2\text{O}$ .

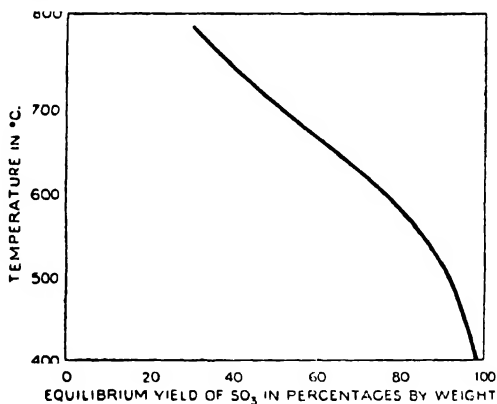
The trioxide is produced when a mixture of the dioxide and oxygen are passed over strongly heated spongy platinum or other catalyst (such as ferric oxide (with or without a little cupric oxide) or some vanadium compound such as oxide or silicate), which effects their combination into the form of white silky needles when condensed in a cooled receiver. Platinized silica gels, under certain conditions, are

stated to be more effective than platinized asbestos, while a satisfactory vanadium pentoxide catalyst is immune to the usual poisons. (See "A New Vanadium-Process Contact Plant" (*C.T.J.*, **88**, 3 (1931)); sulphur trioxide converters in *Ind. Eng. Chem.*, **24**, 1091 (1932).) It is a volatile body which fumes in the air, melts at  $16.8^{\circ}\text{C}$ ., boils at  $44.6^{\circ}\text{C}$ ., and combines vigorously with water, forming sulphuric acid ( $\text{SO}_3 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4$ ), and at the same time evolving much heat. There are two modifications of sulphur trioxide having different vapour pressures.

Two other oxides are less familiar, namely, the sesquioxide ( $\text{S}_2\text{O}_3$ ), formed by the direct union of  $\text{SO}_3$  and sulphur, an indigo-blue crystalline solid, which decomposes at  $70^{\circ}\text{C}$ .; and the heptoxide ( $\text{S}_2\text{O}_7$ ), of m.p.  $0^{\circ}\text{C}$ . and sublimation-point of  $10^{\circ}\text{C}$ ., formed by reaction of ozone and sulphur dioxide.



EQUILIBRIUM CONCENTRATION—TEMPERATURE RELATIONSHIP.



The acids formed from the oxides include hydrosulphurous, sulphurous, sulphuric, and thiosulphuric acids. Other combinations are known as dithionic acid ( $\text{H}_2\text{S}_2\text{O}_6$ ), trithionic acid ( $\text{H}_2\text{S}_3\text{O}_6$ ), tetrathionic acid ( $\text{H}_2\text{S}_4\text{O}_6$ ), and pentathionic acid ( $\text{H}_2\text{S}_5\text{O}_6$ ), and there are corresponding salts.

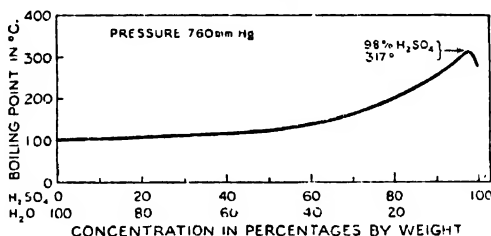
**Hydrosulphurous (Hypsulphurous) Acid** ( $\text{H}_2\text{S}_2\text{O}_4$ ) can be made from sulphurous acid by reduction with zinc, when the hydrogen generated in a nascent state is not evolved, but combines as expressed in the equation:  $2\text{H}_2\text{SO}_3 + \text{H}_2 = \text{H}_2\text{S}_2\text{O}_4 + 2\text{H}_2\text{O}$ . In solution, this unstable acid exhibits a yellowish colour and considerable bleaching properties.

**Sulphurous Acid** ( $\text{H}_2\text{SO}_3$ ) is known only in solution and is somewhat unstable, but less so than the hydrosulphurous acid. It has a strong odour of sulphur dioxide, and gradually undergoes decomposition by atmospheric oxygen. Being dibasic in character, it forms two series

of salts, which are represented by potassium hydrogen sulphite, or acid potassium sulphite ( $\text{KHSO}_3$ ), and potassium sulphite ( $\text{K}_2\text{SO}_3$ ). The various alkaline sulphites are crystalline compounds, obtained by the interaction of sulphur dioxide and an alkali in the presence of water; a hot aqueous solution of the alkali carbonate being treated with the  $\text{SO}_2$  gas until the desired salt is completely formed in solution of the requisite strength, to crystallize out on cooling. The calcium salts are similarly made, using calcium hydroxide ( $\text{Ca(OH)}_2$ ) or the carbonate ( $\text{CaCO}_3$ ).

**Thiosulphuric Acid** ( $\text{H}_2\text{S}_2\text{O}_3$ ) is not known in the free state, being of very unstable character, but it forms well-defined salts, obtained by digesting flowers of sulphur in solutions of sulphites. Sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ ) (incorrectly described as sodium *hyposulphite*, and commonly known as "hypo") is the most important thiosulphate. It can be prepared by the action of sulphur dioxide on sodium sulphide in solution, or by reaction of sodium sulphite solution and sulphur. It is a crystalline body very soluble in water, and largely used in photography in the process known as "fixing"; also as an "antichlor." Potassium thiosulphate can be prepared by the reaction  $2\text{KSH} + 4\text{KHSO}_3 = 3\text{K}_2\text{S}_2\text{O}_3 + 3\text{H}_2\text{O}$ .

$\text{H}_2\text{SO}_4\text{--H}_2\text{O}$  MIXTURES  
BOILING-POINT-CONCENTRATION RELATIONSHIP  
(PRESSURE CONSTANT)



**Sulphuric Acid (Oil of Vitriol)** ( $\text{H}_2\text{SO}_4$ ) is one of the most important sulphur compounds, and is manufactured from sulphur dioxide (1) as produced from the roasting of pyrites (the temperature of combustion ranging about  $1,200^{\circ}\text{C}$ .), or (2) burning sulphur in air; followed by oxidation of the resulting sulphur dioxide by air, either (A) in contact with moisture (water vapour) and using the agency of gaseous nitrogen dioxide, or (B) using a solid catalyst, such as platinum sponge, vanadium pentoxide, or ferric oxide. Sulphur trioxide is produced, which in the presence of water yields sulphuric acid in each case.

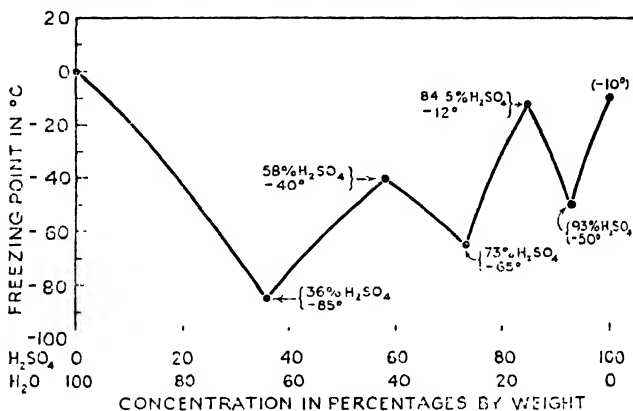
The nitrogen dioxide is obtained from nitric acid, which in turn is produced by the action of strong sulphuric acid ( $\text{H}_2\text{SO}_4$ ) upon sodium nitrate ( $\text{NaNO}_3$ ). In this process, the nitrogen dioxide ( $\text{NO}_2$ ) gives up some of its oxygen, being reduced to nitric oxide ( $\text{NO}$ ), which becomes changed again by the air, regenerating  $\text{NO}_2$ , to serve anew.

An alternative method of supplying nitrogen oxides to sulphuric acid chambers (or mechanically constructed substitutes therefor) consists in the use of a so-called converter, by means of which ammonia (using a gaseous mixture containing 10 per cent. ammonia) is converted into nitrogen oxides. (See Nitrogen Fixation.)

Arsenic and selenium are recovered from the flues of the pyrites burners when these are employed for generating the sulphur dioxide.

### $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ MIXTURES

#### FREEZING-POINT-CONCENTRATION RELATIONSHIP



In the practical manufacture of sulphuric acid, the gaseous sulphur dioxide mixed with air can be "nitrated" by passing the mixture up what is known as a "Glover tower," in which it encounters a stream of nitric acid or nitrated sulphuric acid slowly flowing over flints or other serviceable materials (such as tower-rings, brick, or coke), after which it is passed into leaden condensing chambers of varying construction, into which steam or water (in the form of fine spray) enters, and in which the sulphuric acid is condensed. The out-going current of air carrying nitrous gases is made to pass up what is known as the "Gay-Lussac tower," where it encounters a stream of sulphuric acid trickling over coke packed in the tower, with the result that the nitrous gases are absorbed, and the acid so charged is used over again in the "Glover tower." (See Scrubbing.) Sometimes two Gay-Lussac towers are used, the second one being fed with water instead of sulphuric acid, a modification which is stated to be attended with advantage in the saving of acid. The "Schmiedel box" is part of a sulphuric acid plant that functions in the same way as a "Glover tower."

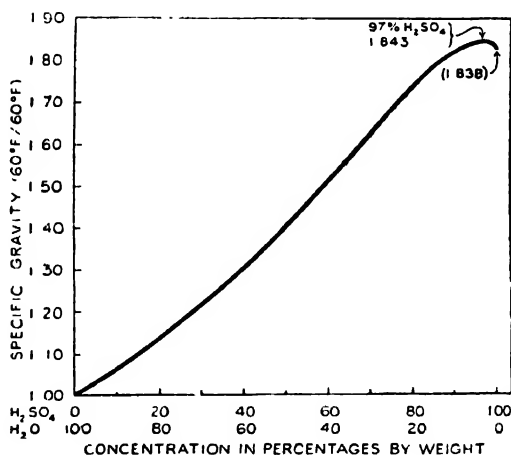
The chambers in which the acid is made are of various forms, including the ordinary rectangular lead-lined chamber, the "Moritz" cylindrical, the so-called "Void" chamber, and the Mills-Packard water-cooled chambers (see a paper by A. M. Fairlie on "Mills-Packard Sulphuric Acid Chambers" in *Transactions of the American Institute of*

*Chemical Engineers*, **33**, 563 (1937)). In the so-called "packed cell" process the gases are forced by a fan into the "Glover tower," and thence into a series of five cells that are lead-sheathed, and packed with acid-resisting bricks, up and down alternately, and from these cells the acid passes to the coolers, the "Gay-Lussac tower" being utilized in the ordinary way. These cells are used to save space, and part of the cost involved by the use of the old-fashioned large lead-lined chambers.

In another patented process (E.P. 231,921; 11.12.23) the burner gases are forced in one direction through sectional flues which replace the "Glover tower" chambers and "Gay-Lussac tower" of the ordinary plant, while sulphuric acid flows by gravity in the reverse direction through a series of pools within the flues. The "Opl tower" system of producing sulphuric acid is very like the "packed cell" method, while in another intensive system of manufacture what is known as the "Duron tower" is employed.

### $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ MIXTURES

#### SPECIFIC GRAVITY-CONCENTRATION RELATIONSHIP



The acid as ordinarily prepared is of about 70 per cent. strength, and is concentrated by evaporation or by passage down a tower in the form of fine spray, in which it encounters a current of hot producer gas which carries off the water, the concentrated acid being collected at the base. The concentration of sulphuric acid for industrial purposes is also effected in heated vessels of lead, glass retorts, platinum stills, cast-iron pots, or by so-called cascade concentrators according to requirements.

Another process of manufacture consists of calcining, at from 1,100° to 1,200° C., a mixture of finely powdered gypsum and coal in definite

proportions, thus yielding a kind of cement and sulphuric acid or oleum at choice. The generation of the sulphur dioxide is promoted by the use of about 4 per cent. ferric hydroxide. This process is modified by the use of aluminous additives, such as clay, slate, or argillite.

Sulphuric acid is also produced as a by-product in the roasting of copper and zinc ores, and from the gaseous effluents from power stations, the complete combustion of the coal used resulting in the production of the acid from the sulphur contained in the fuel. The quantity so obtainable materially affects its production by other processes. In zinc smelters alone, in the U.S.A. in one year, some 900,000 short tons of 60° Bé. (77.7 per cent.  $\text{H}_2\text{SO}_4$ ) sulphuric acid is made.

The dearsenication of sulphuric acid is referred to under the heading of Dearsenicator.

In the pure state, sulphuric acid is a heavy, colourless, oily body of very corrosive properties, having a great affinity for water, and reacting with the oxides and carbonates much in the same way as hydrochloric and nitric acid, thus forming the corresponding sulphates. It finds use in a great number of industrial applications, such as the manufacture of accumulators, alums, celluloid, explosives, dyes, washing soda, glucose, ammonium sulphate, superphosphate, sugar-refining, and in dilute form (1 : 10 or 12) as an insecticide and weed-killer.

In the years 1943 to 1945, inclusive, the consumption of sulphuric acid in the U.S.A. by industries was as follows :

Fertilizer	..	..	..	..	..	29 per cent.
Chemicals	..	..	..	..	..	26 "
Petroleum refining	..	..	..	..	..	11 "
Coal products	..	..	..	..	..	7 "
Iron and steel	..	..	..	..	..	7 "
Paints and pigments	..	..	..	..	..	6 "
Rayon and cellulose film	..	..	..	..	..	5 "
Other uses	..	..	..	..	..	9 "

In 1947 the distribution of the consumption of sulphuric acid and oleum in the United Kingdom and Eire was as follows :

Superphosphates	..	..	..	..	33 per cent.
Sulphate of ammonia	..	..	..	..	15 "
Rayon and transparent paper	..	..	..	..	9 "
Iron pickling	..	..	..	..	6 "
Dyestuffs and intermediates	..	..	..	..	4.5 "
Hydrochloric acid	..	..	..	..	4 "
Paint and lithopone	..	..	..	..	4 "
Sum of above	..	..	..	..	75.5 "
Other industries	..	..	..	..	24.5 "

*Reference :* Lunge's *Acids and Alkalies* (Gurney and Jackson, London).

**Fuming Sulphuric Acid (Oleum)** was originally prepared at Nordhausen in Saxony by the distillation of ferrous sulphate, the gas generated in this way being condensed in ordinary sulphuric acid, so that it really consisted of a mixture of sulphur trioxide ( $\text{SO}_3$ ) and sulphuric acid ( $\text{H}_2\text{SO}_4$ ). The fuming acid can also be produced by the dry distillation of anhydrous sodium bisulphate. It is now made on a rapidly increasing scale by the catalytic or contact process, as referred to already under Sulphur Oxides.

In the Mannheim process the mixture of sulphur dioxide and oxygen (using air) is passed over ferric oxide (which effects the combination to the extent of about 60 per cent.), and then over some suitable material, such as asbestos coated with finely divided platinum, or vanadium silicate maintained at a proper temperature, producing the trioxide ( $\text{SO}_3$ ), which can then be condensed as such or in sulphuric acid in order to concentrate the latter. The platinum when used is deposited on the asbestos, pumice-stone, or other carrier, by soaking it in a solution of platinum and ammonium chlorides and heating to dull redness. In the "Grillo" plant, calcined magnesium sulphate in coarse grains is used as the platinum carrier.

As alternatives to the use of platinum, vanadium and its compounds are cheap and effective catalytic agents. (See the "Selden" contact process in which vanadium catalysts are used (*Ind. Chem.*, 5, 52, 370 (1929)).)

Much of the oleum produced during World War I was obtained by the concentration of the ordinary acid, the requisite quantity of water being evaporated therefrom in towers and cascade evaporators constructed of acid-resisting ferro-silicon or silica basins. A fuming sulphuric acid of any desired strength can be prepared by mixing concentrated sulphuric acid and fuming sulphuric acid of a given strength in the proper proportions.

Sulphuric acid (100 per cent.) has a sp. gr. of 1.984 at  $15^\circ\text{C}$ ., and concentrated acid of  $66^\circ$  Baumé is of sp. gr. 1.8354 and 93.19 per cent.  $\text{H}_2\text{SO}_4$ , and of  $60^\circ$  Baumé is 1.7059 and 77.67, respectively. Twenty per cent.  $\text{SO}_3$ —eighty per cent.  $\text{H}_2\text{SO}_4$  (84%  $\text{SO}_3$ —16%  $\text{H}_2\text{O}$ ) melts at about  $-30^\circ\text{C}$ .; forty per cent.  $\text{SO}_3$ —sixty per cent.  $\text{H}_2\text{SO}_4$  (88%  $\text{SO}_3$ —12%  $\text{H}_2\text{O}$ ) melts at about  $+10^\circ\text{C}$ .; sixty per cent.  $\text{SO}_3$ —forty per cent.  $\text{H}_2\text{SO}_4$  (92%  $\text{SO}_3$ —8%  $\text{H}_2\text{O}$ ) melts at about  $-20^\circ\text{C}$ .; eighty per cent.  $\text{SO}_3$ —twenty per cent.  $\text{H}_2\text{SO}_4$  (96%  $\text{SO}_3$ —4%  $\text{H}_2\text{O}$ ) melts at about  $0^\circ\text{C}$ .; and pure  $\text{SO}_3$ , liquid form, at  $17^\circ\text{C}$ .

**Hydrogen Sulphide (Sulphuretted Hydrogen)** ( $\text{H}_2\text{S}$ ) is an offensive-smelling gas found in nature in volcanic areas; is contained in many mineral waters (such as Harrogate), which are used medicinally.

It is produced by the direct interaction of hydrogen and heated sulphur, and can be prepared by the action of dilute hydrochloric acid (or sulphuric acid) upon ferrous sulphide:  $\text{FeS} + 2\text{HCl} = \text{FeCl}_2 + \text{H}_2\text{S}$ .

A convenient laboratory method of making the gas is by heating together sulphur and paraffin wax in equimolecular proportions, mixed with finely divided asbestos, thus yielding a copious stream of the pure gas.

In liquefied form it boils at  $-59.6^{\circ}\text{C.}$  under atmospheric pressure, while in gaseous form it is colourless, poisonous, soluble in water (to the extent of 4.37 volumes in 1 volume water at  $0^{\circ}\text{C.}$ ), and burns when ignited, producing sulphur dioxide and water:  $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{SO}_2 + 2\text{H}_2\text{O}$ . It forms sulphides by interaction with a number of metals, oxides, and metallic salts, and tarnishes many metals, for example, silver, by direct interaction.

The sulphides of the metals of the alkalis and alkaline earth groups are more or less soluble in water, but the others are insoluble, and used much in analytical chemistry.

**Hydrogen Disulphide** ( $\text{H}_2\text{S}_2$ ), prepared by the action of hydrochloric acid upon calcium or sodium disulphide at a low temperature, is a yellow, heavy, oily body, of sp. gr. 1.376 and b.p.  $74.5^{\circ}\text{C.}$ , capable of dissolving sulphur, and can be used for the vulcanization of rubber in the cold.

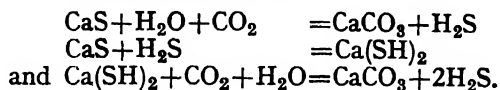
**Sulphur Chlorides** — Sulphur and chlorine by interaction yield several interesting bodies, namely, a monochloride  $\text{S}_2\text{Cl}_2$  and two others, the dichloride ( $\text{SCl}_2$ ), and the tetrachloride ( $\text{SCl}_4$ ), which is a yellow-brown liquid. The first is formed by passing a stream of dry chlorine gas over molten sulphur, when it distils over as an amber-coloured volatile liquid of b.p.  $136^{\circ}\text{C.}$ , and of unpleasant irritating odour. The dichloride is produced by the same process conducted at a temperature not above  $0^{\circ}$ , and is also a dark reddish liquid of much less stable character (b.p.  $59^{\circ}\text{C.}$ ). Both have the property of dissolving sulphur with avidity, and are used for vulcanizing rubber, making rubber substitutes and cements, etc.

**Sulphur Oxychlorides** number five compounds having the formulas:  $\text{SOCl}_2$  (thionyl chloride or sulphurous oxychloride);  $\text{SO}_2\text{Cl}_2$  (sulphuryl chloride or sulphuric oxychloride);  $\text{S}_2\text{OCl}_4$ ;  $\text{S}_2\text{O}_3\text{Cl}_4$ ; and  $\text{S}_2\text{O}_5\text{Cl}_2$ . Chlorosulphonic acid is  $\text{SO}_2(\text{OH})\text{Cl}$ . Thionyl chloride is made by reaction of  $\text{SO}_2$  and  $\text{PCl}_5$ , and has b.p.  $78^{\circ}\text{C.}$  Sulphuryl chloride (see same) is made by combination of  $\text{SO}_2$  and  $\text{Cl}_2$  in the presence of camphor, and has b.p.  $69^{\circ}\text{C.}$  Chlorosulphonic acid is made by reaction of  $\text{SO}_3$  and  $\text{HCl}$ , or of  $\text{H}_2\text{SO}_4$  and  $\text{POCl}_3$ , and has b.p.  $152^{\circ}\text{C.}$

**Sulphur Recovery** — Among other processes devised for the recovery of sulphur from waste gases containing sulphur dioxide, may be mentioned the following: The sulphur dioxide is first absorbed by a basic sulphide, such as calcium sulphide, in the wet or dry state, thus producing calcium sulphite and free sulphur. Subsequently the sulphite is reduced (using hydrocarbon), thus resulting in the regeneration of the calcium sulphide ready for use again.

The "Chance" process for recovery of the sulphur in alkali waste (resulting from the old superseded Leblanc process) is based upon its treatment as mixed into a thin paste with water, with carbon dioxide or lime-kiln gas (which largely consists of that body) under pressure in several successive vessels. The carbon dioxide at first decomposes the calcium sulphide of the waste, liberating hydrogen sulphide, and this passing into the next vessel forms soluble calcium hydrosulphide,

which in turn is decomposed by carbon dioxide, so that a series of interactions is involved as follows :



The sulphuretted hydrogen so generated (in the proportion of two volumes for each one of carbon dioxide), although mixed with atmospheric nitrogen and carbon dioxide, is rich enough to burn into sulphur dioxide, which can be utilized for making sulphuric acid. Alternatively, the gas in admixture with air is passed over a suitable contact mass of iron oxide in the "Claus" kiln, and thus oxidized to water and sulphur:  $2\text{H}_2\text{S} + \text{O}_2 = 2\text{S} + 2\text{H}_2\text{O}$ . (See A. M. Chance, *J.S.C.I.*, 7, 162 (1888).)

Another process depends upon the fact that when sulphur dioxide is passed over sulphide ore the latter is oxidized, ferric oxide and free sulphur resulting therefrom. (See Gas (Coal).)

In America, the recovery of sulphurous gases from smelters is along the line of transformation into sulphuric acid rather than into sulphur. A considerable fraction of the sulphuric acid output is accounted for in this way (see Sulphur (Sulphuric Acid)). In some cases the sulphur dioxide containing gases are purified and liquefied sulphur dioxide is produced.

A highly efficient process of sulphur recovery from waste gases containing only small proportions of sulphur dioxide has been devised by Imperial Chemical Industries, Ltd. The waste gas containing only about 6 per cent. of sulphur dioxide is passed through a cold solution of basic aluminium sulphate which absorbs 6 per cent. of its own weight of the dioxide with an efficiency of 98 per cent. On warming, this solution evolves concentrated sulphur dioxide which, when freed by cooling from water vapour, is passed through a coke reducer at  $1000^\circ\text{C}$ ., whereupon there occurs the exothermic reaction:  $\text{SO}_2 + \text{C} = \text{CO}_2 + \text{S}$ . Any by-products, such as carbon monoxide, carbon oxysulphide and hydrogen sulphide, are brought into action with sulphur dioxide under the influence of a catalyst when the combined sulphur present is liberated.

In a Swedish process applicable to gas rich in sulphur dioxide a specially designed coke gas producer is employed to bring about the following endothermic reaction with a portion of the sulphurous gas:  $\text{SO}_2 + 2\text{C} = 2\text{CO} + \text{S} - 24,000$  calories. The remainder is then added, and the total gaseous mixture passed through heated chambers containing mixed ferric and aluminium oxides. On cooling, liquid sulphur separates.

**Carbon Disulphide** — See Carbon Disulphide.

**SULPHUR BURNERS** — See Sulphur (Oxides).

**SULPHUR DYES** — See Dyes and Dyeing.

**SULPHURETTED HYDROGEN** — See Sulphur (Compounds).

**SULPHURIC ACID** — See Sulphur (Compounds).

**SULPHUROUS ACID** — See Sulphur (Compounds).

**SULPHURYL** — The divalent radical :  $\text{SO}_2$  occurring, for example, in sulphuryl chloride ( $\text{SO}_2\text{Cl}_2$ ).

**SULPHURYL CHLORIDE** ( $\text{SO}_2\text{Cl}_2$ ) — Obtained by the direct union of chlorine and sulphur dioxide at  $30^\circ \text{C}$ ., bone charcoal or activated wood charcoal serving as a good catalyst. Sulphur dioxide and chlorine are continuously dissolved in a body of liquid sulphuryl chloride with activated carbon in suspension at ordinary temperature of the air, the liquid being subsequently filtered off from the carbon. Its preparation is the subject of an article by T. H. Durrans, who found that when the mixed gases are passed into anhydrous alcohol-free ethyl acetate, sulphuryl chloride is readily produced in quantity (*J.S.C.I.*, **45**, 347 T (1926)).

It is a colourless liquid of b.p.  $69^\circ \text{C}$ ., fumes in the air, and is decomposed by water, yielding hydrochloric and sulphuric acids.

It is a vigorous chlorinating agent, and used in the dyeing industry, in the manufacture of acetic anhydride, and for vulcanizing rubber. (See McKee and Salls on sulphuryl chloride (*Ind. Eng. Chem.*, **16**, 279, 351, 833 (1924)); H. C. Brown, "Sulfuryl Chloride in Organic Chemistry" (*Ind. Eng. Chem.*, **36**, 785 (1944)).)

**SULPHYDRATES (Hydrosulphides)** — See Hydrosulphides.

**SUMAC** (*Rhus coriaria*, N.O. Anacardiaceæ) — A tanning material in the form of a greenish powder prepared from the dried leaves and twigs of various shrubs and trees of the *Rhus* order, found in Sicily, Italy, Spain, Greece, U.S.A., etc. The sumac already named and that from Central Italy (*Rhus cotinus*) are the most valued for their tannin content. The *R. cotinus* leaves and twigs yield "young fustic." The American production is obtained from various species, the best known being that described as "white sumac" (from *Rhus glabra*), the berries of which are used in medicine. "Tanners' Sumac" is a name given to the *Coriaria myrtifolia* found in the South of Europe. The tannin content of good sumac ranges from 25 to 28 per cent., and sometimes considerably higher. A brown-coloured extract of  $52^\circ \text{Tw}$ . is prepared commercially, and others of decolourized character are available. It is also used in dyeing, calico-printing, and the manufacture of ink.

**SUMAC WAX** — See Waxes (Japan).

**SUNFLOWER OIL** (from *Helianthus annuus*, N.O. Compositæ) is pale yellow, slow drying, of sp. gr. 0.924, sap. v. 189 to 193; ref. ind. 1.461 at  $60^\circ \text{C}$ ., i.v. 129 to 132; acet. v. 14.5; soluble in alcohol, ether, etc. According to a published analysis it contains 86.6 per cent. unsaturated acids, 7.1 per cent. saturated acids, and its glyceride contents as follows: oleic, 33.4 per cent.; linolic, 57.5 per cent.; palmitic, 3.5 per cent.; stearic, 2.9 per cent.; arachidic, 0.6 per cent.; and lignoceric 0.4 per cent. It is produced in Russia, some 2,700 square miles being devoted to its cultivation; also in China, Italy, the United States, and India. The seeds yield about 22 to 28 per cent. of the oil, and the water-free seeds from 26 to 30 per cent. oil, which is described as a good

lubricant, and when polymerized does not gelatinize ; also said to be as good as olive oil for edible purposes, and used in making soaps, lubricants, varnishes, and illuminants, and for oiling wools.

**SUPA OIL** — From the tree *Sindora Wallichii*, Beuth (Philippine Islands) ; contains a mixture of sesquiterpenes, a crystalline triacontane ( $C_{30}H_{62}$ ), etc.

**SUPER** — A prefix meaning “higher,” and applied to compounds containing comparatively large proportions of some constituent or radical, such as superphosphate of calcium. (See Solution and Solvent Action.)

“**SUPERAM**” — A dry neutral fertilizer prepared by neutralizing the acidity of superphosphate with dilute gaseous ammonia (3 to 5 per cent.), which combines partly with the free phosphoric acid and partly with the phosphoric acid of the monocalcium phosphate ; 97 per cent. of its total phosphoric acid content is said to be soluble in citric acid and 76 per cent. in water.

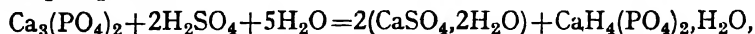
“**SUPERCEL**” — Trade name of an inert and insoluble material for mixing with liquids to assist pressure filtration.

**SUPERLATTICE** — An atomic spatial representation in which various atomic species are in an orderly pattern. Sometimes this situation results from order-disorder reactions (see same) in solid solutions. (See X-Ray Metallography.)

“**SUPERNEUTRAL METAL**” — A silicon-iron alloy suitable for the construction of nitric acid condensers, etc.

**SUPERPHOSPHATE (OF LIME)** is an admixture containing soluble acid phosphate of calcium ( $CaH_4(PO_4)_2$ ), prepared in large quantities for use as a fertilizer, by treating mineral phosphates (such as sombrerite, apatite, and coprolites), bones, etc., after grinding, with about two-thirds of their weight of sulphuric acid of sp. gr. 1.55 to 1.60 (69 per cent.  $H_2SO_4$ ). The grinding of phosphate rock by the so-called “ring and roller” type of mill, which is particularly suitable, gives from 80 to 95 per cent. passing a 100-mesh sieve.

The mixture thus produced is one of calcium sulphate with calcium monophosphate :



but if a larger quantity of sulphuric acid is used, the phosphate is converted into tribasic phosphoric acid, so that the product is of varying composition.

A mixture now generally used consists of 105 parts acid of 115° Tw. or 66.53 per cent.  $H_2SO_4$ , and 100 parts of ground phosphate rock.

Bone charcoal, which has been used for decolourizing purposes as ordinarily prepared by charring bones still retains its calcium phosphate constituents, and can be utilized for the production of “superphosphate.”

## SUPERPHOSPHATE (OF LIME)

## PHOSPHATE ROCK PRODUCTION AND IMPORTS, AND

## SUPERPHOSPHATE PRODUCTION BY COUNTRIES FOR THE YEAR 1936

Authority: *The Mineral Industry of the British Empire and Foreign Countries* (Imperial Institute)

Data arranged and rounded off by the Editor.

	PHOSPHATE ROCK		SUPER- PHOSPHATE PRODUCTION Long Tons
	Production Long Tons	Imports Less Re-Exports Long Tons	
WORLD'S TOTAL ..	11,300,000		
America			
United States ..	3,463,000		3,047,000
Europe			
U.S.S.R. (Russia) ..	2,179,000		1,236,000
Belgium .. ..	171,000 (1935)	304,000	283,000
France .. ..	49,000 (1935)	817,000	1,367,000
Spain .. ..	19,000 (1934)	258,000	453,000
Germany .. ..		1,107,000	935,000
Italy .. ..		758,000	1,311,000
United Kingdom ..		427,000	578,000
Netherlands ..		363,000	467,000
Denmark .. ..		209,000	351,000
Africa			
Tunis .. ..	1,472,000		
Morocco, French ..	1,314,000		
Algeria .. ..	523,000		
Egypt .. ..	523,000		
Asia			
Japan .. ..	111,000	817,000	1,772,000
Oceania			
Nauru Island ..	547,000		
Ocean Island ..	403,000		
Christmas Island ..	155,000		
French Oceania ..	145,000		
Australia .. ..		604,000	1,093,000
New Zealand ..		218,000	347,000

The free phosphoric acid in a good superphosphate should amount to less than 1 per cent., and the water should not exceed 10 to 12 per cent.; the strength being generally expressed in percentage of  $P_2O_5$  soluble in water and in ammonium citrate, but 80 per cent. should be soluble in water.

By the use of phosphoric acid instead of sulphuric acid, "double acid phosphate," containing 40 to 50 per cent. soluble phosphoric oxide, is obtained. It is essentially a monocalcium phosphate  $CaH_4(PO_4)_2$ .

There are grades of phosphates manufactured as fertilizers varying

from 30 to 35 per cent. water soluble; another variety containing 4 per cent. potash is particularly suitable for grass and clover. The idea that superphosphate causes or encourages soil acidity has been demonstrated as mistaken. (See Calcium (Phosphate) for economic data; and Fertilizers.)

**SUPERSATURATION** — See Solution and Solvent Action.

**SUPERSONIC VIBRATIONS** — A paper on the "Industrial Applications of Supersonic Vibrations," by H. Freundlich appears in *Ind. Chem.*, 13, 488 (1937), and the discussion following the same in *Ind. Chem.*, 14, 35 (1938), to which latter is appended an important bibliography.

**"SUPRARENIN"** — See Adrenalin.

**SURAMIN** ("Bayer 205," "Germanin") — One of a series of symmetrical ureas which possess trypanocidal properties and is used in the treatment of sleeping sickness (trypanosomiasis). It is the symmetrical urea of disodium *m*-aminobenzoyl-*m*-amino-*p*-methylbenzoyl-1-naphthylamino-4, 6, 8-trisulphonate; a white powder, easily soluble in water, and insoluble in alcohol. Fourneau 309 ("Moranyl") is probably identical with Suramin.

**SURFACE ACTIVE AGENTS** — See Colloid Chemistry, Detergents, Emulsions, and Surface Tension.

**SURFACE CHEMISTRY** — See Colloid Chemistry, Catalysis, Emulsions, and Lubrication.

**SURFACE TENSION** — The molecules which make up the surface layer of a liquid are acted upon by unbalanced forces which tend to cause the surface area of the liquid to contract as though it were surrounded by a rubber-like membrane under tension. As a result of this tendency to contract, the liquid is said to exhibit surface tension and it is possible to ascribe to it a definite value indicative of the magnitude of the tension.

A molecule *in the interior* of a liquid is completely surrounded by other liquid molecules so that in general it is equally attracted in all directions. On the other hand, a molecule *in the surface* of a liquid is attracted much more strongly on the inward side, because the concentration of the molecules in the liquid phase is much greater than their concentration in the vapour phase, and as a result the surface of the liquid tends to be pulled inward and to contract to the smallest possible area. For these reasons a drop of liquid tends to become spherical.

In order to extend the surface area of a liquid it is necessary to do work to bring molecules from the interior of the liquid into the surface against the inward attraction forces of the liquid. The work necessary to increase the area by a unit amount is called the free surface energy, and is equal to the surface tension, which is the energy opposing an increase in surface area. The surface tension is the same at every point and in all directions along the surface of the liquid. The surface tension is defined as the force in dynes acting at right angles to any line of one centimetre length in the surface. Although the free surface energy is probably the fundamental property of the surface, it is often

convenient to replace it by the surface tension ; the equivalency of the two quantities makes this justifiable.

Surface tension can be determined by : (1) measuring the rise of a liquid in a capillary tube ; (2) measuring the pressure necessary to form a bubble in the liquid under controlled conditions ; (3) measuring the mass of a drop of liquid falling from a standard tube under controlled conditions ; (4) measuring the force necessary to pull a platinum wire ring from the surface of a liquid. All these methods must be carefully controlled, and lend themselves to a determination of relative surface tension more easily than to absolute surface tension. Tables I and II show the surface tension for some liquid materials.

In general surface tension varies inversely with temperature, that is, the surface tension decreases as the temperature increases. When two liquids whose surface tensions do not differ greatly are mixed the surface tension of any mixture of the two is nearly a straight-line function of the concentration. If the surface tension of the two liquids differs greatly, however, the addition of small amounts of one liquid into the other causes marked changes in the surface tension. Electrolytes generally increase the surface tension of water but to a very small extent.

For further application of surface tension see Adsorption, Detergents, Parachor, and Vapour Pressure.

TABLE I  
SURFACE TENSION OF MOLTEN METALS AT STATED TEMPERATURES

Molten Metal	Temperature, ° C.	Surface Tension Dynes per cm.
Copper .. .. .	1,200	1,160
Gold .. .. .	1,200	1,120
Silver .. .. .	1,000	923
Zinc .. .. .	900	770
Mercury .. .. .	20	485

TABLE II  
SURFACE TENSION OF LIQUIDS AT 20° C.

Liquid	Surface Tension Dynes per cm	Boiling Points, ° C.
Water .. .. .	72·8	100
Nitrobenzene .. .. .	41·8	210·9
Carbon disulphide .. .. .	33·5	46·3
Benzene .. .. .	28·9	80·1
Toluene .. .. .	28·4	110·8
Acetic acid .. .. .	27·6	118
Chloroform .. .. .	27·1	61·3
Carbon tetrachloride .. .. .	26·8	76
Acetone .. .. .	23·7	56·5
Methyl alcohol .. .. .	22·6	64·6
Ethyl alcohol .. .. .	22·3	78·5
Ethyl ether .. .. .	17·0	34·6

**"SURFACTANTS"** — A term coined and registered to describe those substances that markedly lower the surface tension of liquids, generally water, thus permitting greater penetration, for example, into crevices and pores. (See Colloid Chemistry, and Soaps.)

**SUSPENSIDS** — See Colloid Chemistry.

**SWEAT** — Exudation from the skin, being water containing about 2 per cent. solid matters, including sodium chloride, acetic, butyric, formic, lactic, and other acids, fatty matters, and some other excretory products.

**SWEET POTATO** (*Ipomœa batatas*, Poir, N.O. Convolvulacæ) — A tropical climbing plant, the thickened roots of which contain much starch. So-called "Natal cotton" is obtained from the seeds of another species of batatas.

**SYLVANITE** (Graphic Tellurium) — A gold, silver, and tellurium ore ((Ag,Au)Te<sub>2</sub>) found in Transylvania, Colorado, and elsewhere; crystal system No. 5, and sp. gr. 5.7 to 8.3.

**SYLVESTRENE** (Carvestrene, D-Sylvestrene) (C<sub>10</sub>H<sub>16</sub>) — A monocyclic diolefin terpene, which has been synthesized from *meta*-cresol, but is usually obtained from Swedish turpentine. It also occurs in pine-needle oil (*Pinus Sylvestris*), hence its name. It does not occur pre-formed in nature, an isomeric diterpene, carene, C<sub>10</sub>H<sub>16</sub> being converted into sylvestrene by the hydrochloric acid used during the preparation of the latter. (See Simonsen, *The Terpenes* (Cambridge University Press); Essential Oils, and Hydrocarbons (Terpenes).)

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**SYMMETRY** — See Crystals, Dipole Moment, and Isomerism.

**SYMPATHETIC INK** — See Inks, and Cobalt Compounds.

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**SYNTANS** — See Tanning.

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**SYNTHESIS** — The chemical building up or construction of elements into compounds, or of compounds into more complex bodies (not neces-

sarily the reverse of analysis or decomposition). The production of rust upon iron is an act of synthesis, by which the oxygen and other constituents of the air enter into chemical combination with the iron ; and the formation of verdigris on copper exposed to damp air is another act of synthesis. When hydrogen gas is burned in the air it forms water synthetically by chemical combination with the atmospheric oxygen. When lime is exposed to carbon dioxide gas, they enter into combination, forming calcium carbonate by synthesis.

The use of the term synthesis is often restricted to the syntheses carried out by chemists in the laboratory, as opposed to the natural means of synthesis employed by plants and animals. Until 1828 it was believed that only "inorganic" compounds could be prepared artificially, and that the "organic" compounds could only be synthesized by nature, a "vital force" being necessary for the process. The preparation in that year, by Wöhler, of urea from the typically inorganic ammonium cyanate finally delivered a mortal blow to this doctrine, and since that time more compounds have been synthesized by man in the laboratory than by nature in the whole period of organic evolution.

The preparation of the hitherto unknown elements, such as francium, americium, and plutonium, may be regarded as the crowning achievement of man's powers of synthesis ; while the debt that modern medicine owes to chemistry for such substances as mepacrine, suramin, paludrine, heptalgin, and dozens of other chemotherapeutic agents cannot be computed. Hundreds of synthetic dyes have now taken the places of such substances as indigo and madder, and the natural textiles have been supplemented by rayon, nylon, viscose, etc. The uses to which the synthetic resins have been put are legion, and examples of synthesis are encountered in many places.

**SYNTHETIC PETROL** — See Fuel (Liquid), and Motor Spirit.

**SYNTHETIC RESINS** — See Gums and Resins.

**SYNTONIN** — An acid albumin insoluble in water, prepared from muscle fibrin by the action of dilute hydrochloric acid.

**SYRINGIN** — See Glycosides.

**TABLE SALT (Common Salt)** — See Sodium (Chloride).

**TACHYDRITE** — A magnesium calcium salt ( $2\text{MgCl}_2, \text{CaCl}_2, 12\text{H}_2\text{O}$ ), occurring in the Stassfurt deposits ; crystal system No. 3, and sp. gr. 2.0.

**TACONITE** — Ferruginous cherts occurring in the iron-ore beds of the Lake Superior region (U.S.A.). Work on the preparation of taconite for industrial use as iron ore involves sintering and nodulizing. The total beneficiation programme involves mining, separation of fine material, and cementing this material into nodules.

**TAIFUSHI OIL** — A fixed oil, official in the Japanese pharmacopœia as *Oleum Gynocardiaë* (*Oleum Chaulmoogræ*), consisting mainly of the glycerides of chaulmoogric and hydnocarpic acids, together with some palmitin; obtained from the seeds of *Hydnocarpus anthelmintica*; sp. gr. 0.94 to 0.95; m.p. 26° to 29° C.; sap. v. 191 and i.v. 88 to 90 (Hanus). (See Chaulmoogra Oil, and Hydnocarpus Oil.)

**TALC** ( $3\text{MgO}, 4\text{SiO}_2, \text{H}_2\text{O}$ ) — A mineral of crystal system No. 4, and sp. gr. about 2.5 to 2.8, deposits of which are found in Scotland, Canada, the United States, Italy, Spain, Norway, etc., composed of hydrous magnesium silicate, published analyses of which are as follows:

						Per cent.	Per cent.
SiO <sub>2</sub>	..	..	..	..	..	63.2	63.5
MgO	..	..	..	..	..	28.0	31.7
Moisture, etc.	..	..	..	..	..	8.8	4.8
						100.0	100.0

The most valuable type is stated to occur in the Madoc area of Ontario, and is of sufficient purity for use in making toilet preparations and finishing of laces, etc., while the commoner variety, known as soapstone, is sometimes used as a lining for furnaces.

The more laminated varieties, being transparent and incombustible, are of considerable utility for making stove-windows, goggles, lamp chimneys, and phonograph diaphragms.

Talc powder, pearly in appearance and unctuous to touch, forms a very nice absorbent basis, and the higher grades are used in preparing toilet preparations; others, in crayon form, are used in making French chalk and for lubricating, but about 90 per cent. of the talc mined is ground to flour and used in the manufacture of opaque paper, moulded rubber goods, foundry facings, and in the roofing trade. "Indurated talc" or "talc slate" is a variety which is not of laminated character, but resembles steatite and is used similarly. (See French Chalk, Soapstone, and Steatite.)

**TALCUM** — See Magnesium (Silicate).

**TALL OIL** — The Swedish name for pine oil is "tallolja," which in Germany was changed to "tallöl." Since the oil referred to is not the "pine oil" of English-speaking regions, the name "tall oil" is used. It is obtained by acidifying the soap separating from black-liquor in the sulphate-cellulose ("Kraft") process for making wood into paper pulp. The uses are in paint and varnish, linoleum, soap, lubricants, and flotation agents for minerals. It can be split into high-grade rosin and into fatty acids. (See Cellulose, and Paper.)

**TALLOW** — The name applied to the harder varieties of fats, such as the suet of the ox and sheep and the vegetable cacao fat. It is separated from the cellular tissue, with which it is associated in suet, by melting.

Beef tallow has a sp. gr. 0.943 to 0.952, sap. v. 193 to 200, and

i.v. 38 to 46. Mutton tallow has a sp. gr. 0.937 to 0.953, sap. v. 192 to 195, and i.v. 35 to 46. Tallow melts at from 41.2° to 52° C., has a ref. ind. of 1.451 at 60° C., and consists of a mixture of glycerides.

A sample of mutton tallow showed the mixed fatty acids to consist of myristic, 4.6 per cent. ; palmitic, 24.6 per cent. ; stearic, 30.5 per cent. ; oleic, 36.0 per cent. ; and linolic, 4.3 per cent.

Tallow is used in process engraving and the leather trade, also for making soaps and candles. (See Fats, and Vegetable Tallow.)

**TALLOW-SEED OIL** (*Stillingia* Oil) — See Vegetable Tallow.

**TAMARIND** — The preserved pulp of the fruit of *Tamarindus indica*, N.O. Leguminosæ (East and West Indies), cultivated in many warm countries and containing citric, tartaric, and malic acids, etc. ; used in medicine as a laxative, and in sauce-making.

**TANNASE** — The name given to the active principle (of presumably enzymic character) secreted or formed by certain mould fungi, notably *Aspergillus niger* and *Penicillium glaucum*, which effects the decomposition of gallo-tannin, gallic acid being produced quantitatively. Yeast secretes a similar principle. (See Alcohols (Amylo Process).)

**TANNIC ACID** — A tannin obtained from specially fermented oak-galls by extracting them with water-saturated ether. It usually occurs as a pale-brown powder, with a characteristic odour and an astringent taste, and is readily soluble in alcohol, water, and acetone. Aqueous solutions yield a blue-black colour with ferric chloride, and a precipitate with gelatine, proteins, salts of the heavy metals, and most alkaloids. Chemically, tannic acid is penta-*metadigalloyl*-glucose, and on hydrolysis with sulphuric acid yields gallic acid and glucose. Its minimum molecular formula is  $C_{76}H_{52}O_{46}$ , and it behaves as a colloid in aqueous solutions. It is used in medicine as an astringent, but is no longer recommended as a burn-dressing owing to the permanent contraction of the tissues which occurs when it is used over large areas. (See Gallic Acid, and Tannins.)

**TANNING** is an important industry. The annual value of leather tanned in the United States is of the order of \$400,000,000 (1939), and of £30,000,000 in the United Kingdom. "Kips" of intermediate size are the hides of small East Indian buffalo. The common method of curing hides is that of dehydration by use of common salt, and unless the hides are thoroughly clean its penetration is more or less prohibited, thus giving rise to or promoting the affection known as "read heat," brought about by action of halophilic bacteria. This trouble can be more or less obviated by the use of a small proportion of naphthalene mixed with the salt.

The operations involved in practical tanning vary widely, and the following notes give only a general account. After soaking to soften and to remove blood and lymph, sheep skins are painted on the fleshy

side with a mixture of slaked lime and sodium sulphide or calcium hydrosulphide, and then the wool is pulled, leaving the skin, or "pelt." Attention has been drawn to the advantage of using calcium chloride as an addition to sodium sulphide depilatory mixture. After washing, the pelts are steeped for some days in lime liquor, and, after rubbing off the hair, subjected to a mechanical operation ("fleshing") to remove all adhering flesh. After careful washing to remove the lime as far as possible, the skins are ready for "bateing" or "puering," to render them soft and supple by removal of hair sheaths, sebaceous glands, muscles, sweat ducts, etc., held together by elastic fibres, a process which is of a fermentative character, carried out by dressing with dog or fowl dung or other material comprising tryptic enzymes and several synthetic substitutes. Another mixture for bateing consists of 65 per cent. ammonium chloride with wood-fibre, dry pancreas, and a little castor oil.

"Liming" hydrolyses proteins to peptones in the first stage, and the bacteria contained in old limes cause further hydrolysis to amines and amino-acids, so that this action approaches that of "bateing," which hydrolyses the proteins to polypeptides, peptides, and amino-acids, which take no part in the tanning process.

Both the red sulphide of arsenic (realgar) and the yellow sulphide (orpiment) can be used in place of sodium sulphide in connection with the liming process, but as they are not soluble by themselves, the lime has first of all to be slaked, and then the arsenical sulphide is added, thus producing a mixture which has very similar effects to those produced by sodium sulphide. It has been ascertained that the addition of ammonium chloride or sulphate or common salt in small proportions increases the activity of the proteolytic enzymes in the bateing process.

After drenching in a fermenting infusion of bran, the skins are ready for treatment with the **tan liquor**, which may be an infusion of sumac, other tanning materials which are used being barks, gambier, myrobalans, valonia, and extracts, such as kino, and those of oakwood, chestnut, and quebracho. Borax can also be used as a soft antiseptic soak, in common with boric acid, in course of deliming. The addition of hydrochloric acid, lactic acid, or sulphuric acid to the tan liquors with the object of neutralizing lime carried over from the liming process has proved beneficial.

The preliminary wet treatment of hides and skins involves complicated enzymic and bacterial action, freeing the so-called collagen which has been described as "an aggregate of *cyclo*-peptide micelles." In the process of tanning, the astringent principles enter into combination with the collagen (gelatinous or protein) part of the skins constituting the fibrous tissues, thus producing leather.

"Chamoising" of skins really consists of two processes—viz., one in which the collagen is converted into a non-hydrolysable body (or tannage properly so called), and a "filling" process by adsorption to lubricate the leather.

The so-called quinone tannage is carried out by use of such substances as benzoquinone, toluquinone, and naphthaquinone, these having the

property of producing compounds of high molecular weight. In one modification of the process quinol in presence of alkali is used, while in another patented process chloranil is employed.

The rough tannage of pelt by means of smoke is chiefly attributable to its formaldehyde and phenolic constituents.

Formaldehyde has been used in tanning, by reason of its coagulating and preservative effect on the collagen molecule, and a preliminary treatment of this sort does not interfere with the subsequent absorption of chromium as next referred to.

According to a French patent, satisfactory tannage of hides can be effected by soaking in a 10 per cent. solution of hydrofluosilicic acid.

**Chrome Tanning**—In this process, chromium salts are used for treatment of the prepared pelts, the bath consisting of a mixture of potassium or sodium dichromate with hydrochloric or sulphuric acid, followed by the application of sodium thiosulphate to effect the reduction of the chromium salt for combination with the tissue. After unhairing and pickling by immersion in a bath of dilute sulphuric acid and sodium chloride, skins can be completely tanned in two days by immersion in a bath of chrome liquor, consisting of basic chromic sulphate diluted to contain 17 grams of chromic oxide ( $\text{Cr}_2\text{O}_3$ ) per litre.

The impregnation of the materials to be tanned is sometimes effected by electric endosmosis, which is said to be available for the impregnation, with chromium or other metallic salts, of fabrics which have been treated with glue or gelatine. This method permits of the utilization of very dilute tanning liquors and greatly facilitates the process in point of time. The nature of this process has been described as a precipitation of the positively charged micellions of chromium hydroxide by the oppositely charged colloidal protein hide substance.

Unmordanted chrome leather is stated to have a greater affinity for acid and direct coal-tar dyestuffs than vegetable leather. The composition of chrome-tanned leather waste, with a water content of 50 per cent., is given as approximately—protein, 35 to 40 per cent. ;  $\text{Cr}_2\text{O}_3$ ,  $2\frac{1}{2}$  to  $3\frac{1}{2}$  per cent. ;  $\text{SO}_3$ , 1 to  $2\frac{1}{2}$  per cent.

**Artificial Leather** is the name given to a number of composite materials made of any suitable base (such as cotton cloth, felt, or paper), coated with plastic masses of solutions of nitrocellulose, castor oil, and pigments in successive layers, the volatile solvents of the plasticizers being subsequently evaporated. Such products may be given an embossed covering in imitation of grained leather. Pyroxylin dissolved in amyl acetate can be used in admixture with castor oil ; also other varieties of nitrated cellulose ; blown linseed and other oils can be used in place of or in addition to castor oil ; and a great variety of solvents are available, whilst pigments are introduced to give colour and body to the coverings.

**Leather scrap** has been used to some extent as a fertilizing agent, but the presence of chromium compounds is dangerous to vegetation, and other methods of disposal have been suggested, including destructive distillation, which yields a carbon black as final residue, from which the chromium can be recovered as chromic oxide after burning in a current of

air, and from the distillate it is possible to extract ammonia, pyrrole, etc.

*References* : "Chemistry of the Tanning Process," being a report of discussion before the British Association for the Advancement of Science (*Chem. Age*, 29, 273 (1933)); D. J. Law on "Modern Light Leather Manufacture" (*J. Inst. Chem.*, 1933, Pt. 3, 182); H. G. Bennett on *Animal Proteins* (Baillière, Tindall and Cox, London); *Practical Tanning*, by A. Rogers (Crosby Lockwood and Sons, London); *Leather Manufacture*, by A. Watt (Crosby Lockwood and Sons, London); *Modern Practice in Leather Manufacture*, by J. A. Wilson (Reinhold Publishing Corp., New York); *Practical Leather Chemistry*, by A. Harvey (Crosby Lockwood and Sons, London); *The Chemistry of Leather Manufacture*, by G. D. McLaughlin and E. R. Theis (Reinhold Publishing Corp., New York); Leather Cloth, Osmosis, Pyroxylin, Tannins, and Tawing.

**TANNINS**—A generic name given to astringent principles of the bark and some other parts of trees and shrubs (such as algarobilla, canaigree, chestnut, divi-divi, the dogo tree of the Fijian Islands, eucalyptus, gambier, hemlock, larch, mangrove, mimosa, oak, osage, pine, quebracho and sumac), which combine with the collagen of animal hides to form leather. In Australia, wattle bark is the principal tanning agent employed by tanners, that of the golden wattle (*Acacia pycnantha*) and the black or green wattle (*A. decurrens*) being two of the more important varieties. Valuable tan barks are yielded by the *Eucalyptus diversicolor* (Karri bark), the mallee (*Eucalyptus occidentalis*), and other varieties of eucalyptus tree. Among tanning barks from Madagascar there are Rotra bark (*R. fotsy* and *R. meno*), containing 12.62 per cent. soluble tannins; Lalona (*Weinmannia bojeriana*), containing 13.75 per cent.; Filao (*Casuarina equisetifolia*), containing 15.31 per cent.; and Badamier bark (*Terminalia catappu*), containing 11.81 per cent. soluble tannins. The principal tannin is the so-called tannic acid. The astringent principles common to cutch and mimosa extract are either glucosides or associated substances of that nature, as both yield an unfermentable sugar upon hydrolysis. (See Tannic Acid.)

Tan substances can be roughly classified as (1) "catechol tannins," including birch bark, gambier, oak bark, quebracho, mimosa bark, mangrove, mallee bark, catechu, and hemlock, which yield catechol under the influence of heat, and (2) "pyrogallol tannins," including myrobalans, valonia, oakwood, sumac, chestnut, algarobilla, and babool, which yield pyrogallol under the influence of heat (J. A. Reavell).

To prepare the extractives, the materials are subjected to crushing and leaching operations, so that, for example, 100 tons of mimosa bark will yield 100 tons of liquid extract containing 30 per cent. of so-called tan. Freshly cut western hemlock (*Tsuga heterophylla*) bark is stated to contain from 9 to 15.5 per cent. tannin, and that of spruce (Sitka) from 12 to 17.5 per cent. of the dry substance, the larger contents being found in summer.

## SOME REACTIONS OF TANNINS

Reagent	Catechol Class	Pyrogallol Class
Bromine water excess	Yellowish to brownish precipitate	No precipitate
Ferric salt solution	Greenish-black colour	Dark blue colour
Water infusion of tannin plus concentrated sulphuric acid stratified	Dark red or crimson layer at junction. Upon diluting with water, turns pink	—
On leather	No bloom	Bloom formed

A crystalline glucoside-tannin isolated from the seeds of *Paullinia cupana* has been assigned the composition represented by the empirical formula  $C_{38}H_{36}O_{20}$  or  $C_{37}H_{35}O_{18} \cdot COOH$ . Another crystalline tannin of the nature of a sugar ester, from the leaves of the *Acer ginnala*, named acertannin, is reported to have the composition  $C_{20}H_{20}O_{13}$ , and yields gallic acid ( $C_7H_6O_5$ ) and aceritol ( $C_6H_{12}O_5$ ) upon hydrolysis. M. Tsujimura claims to have isolated from green tea a tannin of the composition  $C_{22}H_{18}O_{10} \cdot 2H_2O$ . Hamamelitannin is the name given to a crystalline body of the composition  $C_{20}H_{20}O_{14} \cdot 6H_2O$ .

The tannin of the oak is an amorphous, reddish-yellow, acidic material, freely soluble in water, alcohol, and acetone, and its general nature is that of a glucoside. There is said to be a difference between the tanning properties of the natural oak bark and the extracts, due to the presence of enzymes in the former and absence in the extract, which are credited with the property of splitting up the larger tannin complex into a simpler substance more suitable for leather-making.

**Synthetic Tannins** — A number of so-called synthetic compounds are now used, some of which are of the nature of simple natural tannins, while others have nothing in common beyond the fact that they behave like them in contact with animal pelt. One of these latter is a body known as "Nerodol D" (dicresylmethanedisulphonic acid), another "Nerodol N" (dinaphthylmethanedisulphonic acid). There are other products produced by the condensation of the sulphonic acids of the higher hydrocarbons, as also phenols and cresols with formaldehyde, many of which are applicable to tanning; some of them, it is alleged, possessing advantages over vegetable products. It is not suggested that the new synthetic bodies ("syntans") will replace the natural tannins, but rather supplement them, a combination offering in many cases certain advantages. It is alleged that the synthetic compounds, used in the early stages of tanning in conjunction with natural extracts, help in the rapid penetration of the natural tan, thus shortening the process duration. Some of them are also of value as bleaching agents, and remove iron and salt stains, but before they can be safely used, it is important to ascertain to what extent they may be destructive of hide substance.

**Testing** — It has become customary to determine as tannin that portion of the water-soluble constituents of vegetable materials which will precipitate gelatine from solution, and will form compounds with hide-fibre resistant to washing, but A. E. Jones has shown that "a positive gelatine test is no specific indication" of tannins, because such substances as gum arabic and inulin are also precipitated by gelatine.

The iron and ammonium citrate of the *British Pharmacopæia*, together with ammonium acetate, has been advocated as the best test for real tannins, causing their complete precipitation from plant extractions. The use of cinchonine sulphate as a determinant is referred to under the head of Cinchona (Cinchonine). Hide-powder is collagen modified by liming, and the comparative tanning properties of various materials is determined by a hide-powder test.

## ANALYSES OF SOME TANNINS

By C. Ainsworth Mitchell (*Analyst*, 48, 14 (1923)).

	Moisture Per cent.	Total Extract Per cent.	Tannin Per cent.	Gallic Acid Per cent.	Total Pyrogallol Equiva- lent Per cent.
Valonia .. ..	13.15	49.0	46.0	3.0	17.3
Divi-divi .. ..	11.49	74.0	32.8	2.6	12.66
Commercial gall liquor	97.32	2.68	1.6	0.2	0.66
Commercial myrobalan liquor .. ..	97.08	2.92	1.62	0.5	0.87
Chinese tea .. ..	—	—	3.32	0.84	1.66
Tea (blend) .. ..	—	—	7.9	0.8	2.8

Spent tan-bark is used in the manufacture of white-lead by the old Dutch process, and is of course available as fuel when suitably dried. There is also a patented process for utilizing spent tan as a reducing agent in the manufacture of one-bath chrome-tanning liquors. (See Catechu, Tannase, Tannic Acid, Tawing, and Lead (White Lead).)

**TANSY OIL** — The volatile oil distilled from *Tanacetum vulgare*, a herb indigenous to Europe and Great Britain. It is a thin, yellowish oil, darkening rapidly on exposure to air and contains thujone, camphor and borneol; soluble in alcohol and ether; sp. gr. 0.925 to 0.955 at 15° C.; opt. rot. +25° to +45° at 20° C.

**TANTALITE (Columbite)**  $((\text{Fe}, \text{Mn})\text{O}(\text{Cb}, \text{Ta})_2\text{O}_6)$  of crystal system No. 4, and sp. gr. 7 to 8. (See Columbium.)

**TANTALUM (Ta) and its Compounds** — Atomic weight 180.88. See Elements for other data. Tantalum is a rare metallic element found

in nature in association with columbium in some Australian and Swedish minerals and in many other countries, including tantalocolumbates, which, as also the titanocolumbates, are of great complexity.

Tantalum is commercially available of 99.9 per cent. purity ; is a little darker than platinum ; is nearly related chemically to vanadium, but its use in making electric lamp filaments has been largely superseded by that of tungsten. It is not tarnished by air, nor attacked by acids, other than hydrofluoric acid ; it combines with carbon to form a carbide, and at a red heat combines with hydrogen, with nitrogen, and with chlorine. The metal is made by heating the double fluoride of tantalum and potassium in an electric furnace.

The tensile strength of tantalum is about  $2\frac{1}{2}$  times that of hard platinum. As the metal combines softness with workability, and exhibits great resistance to wet corrosion, it finds employment in place of platinum for making laboratory basins, etc., also in electrolytic rectifiers and other applications, and is superior to all other metals for manufacture of electrodes of high vacuum tubes. Tantalum metal is used in surgery since it is the only metal to which flesh will grow, also, due to its remarkable resistance to hydrochloric acid, it is used—either as thin tantalum or as tantalum-clad steel—in apparatus containing this chemical. C. W. Balke discusses tantalum in *Ind. Eng. Chem.*, 27, 1166 (1935) ; and see also *Rarer Metals*, by Jack DeMent and H. C. Dake (Chemical Publishing Co., Brooklyn).

There are three **oxides** of tantalum, namely, the pentoxide ( $Ta_2O_5$ ), a white solid ; the tetroxide ( $Ta_2O_4$ ), a dark grey solid ; and the dioxide ( $TaO_2$ ), a brown powder.

**Tantalum Chloride** ( $TaCl_5$ ) is a light yellow solid, of m.p.  $221^\circ C.$ , and b.p.  $242^\circ C.$ , and the **bromide** ( $TaBr_5$ ) has similar properties.

**Tantalum Nitride** ( $Ta_3N_5$ ) is mentioned under Abrasives.

“ **TANTIRON** ” — A hard and brittle brand of acid-resisting silicon-iron alloy ; m.p. about  $1,200^\circ C.$  ; density 6.9.

**TAPIOCA** — A starchy body, useful as food, obtained from the roots of *Jatropha Manihot* (*Manihot utilissima*), of the N.O. Euphorbiaceæ, cultivated in the West Indies and by the Chinese in Malaya. The flour contains some 75 to 80 per cent. of digestible carbohydrates, and is used for starch-making, as an adhesive, and in the textile industry. A similar product is known as *juca* or *yucca*. The name of tapioca is sometimes given to an Indian variety of granulated sago which is obtained from an entirely different plant. There are varieties of tapioca known as “sweet” and “bitter,” the last named containing a larger content of hydrocyanic acid or cyanogenetic glucosides present in the flesh and cortex of the “bitter” variety, but only found in the cortex of the “sweet” variety. (See Cassava, and Manioc.)

**TAR** — As shown in the article on Coal, the characters of tars and their decomposition products necessarily vary according to the nature of the raw materials from which they are produced and the

temperatures and other conditions under which they are subjected to distillation.

In the "T.I.C." (lead bath) process of tar distillation a cushion of lead is placed on the still bottom, and the layer of tar is only about  $\frac{1}{2}$  inch in thickness, the process depending upon the rapid transference of heat enabling large throughputs to be obtained with continuous operation. Carbon growth on the still bottom is said to be thus prevented, and the tar so rapidly dehydrated that "priming" and consequent fire risk are avoided. There is an adequate arrangement for dealing with the pitch that results from the process.

When coal is heated out of contact with air, a point of temperature ranging from 230° C. (for brown lignites) to 330° C. (for bituminous coal) is reached when decomposition is made evident by the rapid evolution of gas, and at this stage "primary tar" is formed. In high-temperature carbonization in gas retorts or coke ovens, the primary tar vapours become heated to from 800° to 1,100° C., and thereby undergo "cracking," thus giving rise to the production of further gases and the secondary or ordinary gas-tar.

The tar from vertical retorts differs in many respects from that obtained from the older horizontal retorts; the pitch resulting from its distillation is said to be less valuable for briquette making; the yields of benzol, toluol, and xylol are stated to be low, while the yields of cresote, pyridine, and tar acids are superior, although the separated tar acids, when extracted, undergo rapid discoloration and are therefore not so suitable for use in making disinfectants, etc.

All high-temperature coal tars and the pitches derived from them contain varying percentages of free carbon resulting from decomposition of the volatile matter of the coal. For obtaining briquetting pitch the final tar temperature should not be above 280° to 300° C., and the time of exposure should be reduced to a minimum.

The distillation method of separating tar constituents leads to from 30 to 60 per cent. pitch, whereas the solvent method cuts down the ill-defined materials to about 6 per cent.

Low-temperature tars are of more complicated composition than those obtained by high-temperature carbonization, and have a high content of tar acids making up from 10 to 30 per cent. of the total tar. Morgan, Pratt, and Ross have made a careful chemical study of low-temperature tar derived from coal of the Kinneil 6-ft. seam, and among other results have found that it contains a notable proportion of resinous products of varied nature which are likely to find industrial application.

The solvent method of separation of tar constituents has shown that these resinous bodies (resinenes), which disappear at higher temperatures, are accompanied by neutral oils, bases, phenols, and carboxylic groups, while the amount of naphthalene increases with rise of temperature.

Low-temperature tars vary in specific gravity from 0.85 to 1.05 and have a calorific value of 16,500 to 17,000 B.Th.U. They can be used as fuel in Diesel engines after removal of the tar acids, and are reported

to be of special value for the treatment and preservation of wood and other purposes. The hydrogenation of coal and the products of its low-temperature carbonization products is referred to under the heading of Coal.

The British Road Tar Association's specification provides that tar No. 1 for surface tarring and No. 2 for making tar macadam should fall respectively within the requirements as follows, blast furnace tar being excluded and the tar from manufacture of carburetted water-gas being limited to a content of 10 per cent. :

	Tar No. 1	Tar No. 2
Sp. gr. at 15° C., not higher than ..	1.225	1.240
Sp. gr. at 15° C., not lower than ..	1.140	1.150
Water or ammoniacal liquor (per cent. by weight) .. .. .	0.5	0.5
Other distillate (light oils) below 200° C., not more than (per cent. by weight)	1.0	1.0
Distillate between 200° and 270° C. (middle oils), within the range (per cent. by weight) .. .. .	9.5 to 21.0	8.0 to 16.0
Distillate between 270° and 300° C. (heavy oils), within the range (per cent. by weight) .. .. .	3.5 to 12.0	3.5 to 12.0
Phenols or crude tar acids, not more than (per cent. by volume) ..	5.0	4.0
Naphthalene, not more than (per cent. by weight) .. .. .	6.0	5.0
"Free carbon," not more than (per cent. by weight) .. .. .	20.0	6.0 to 21.0
Consistency or viscosity, within the range (seconds) .. .. .	10 to 40	40 to 125

The consistency or viscosity to be determined by the standard consistometer at 30° C. or the equivalent on other instruments. Copies of other specifications can be obtained from the B.S.I. (B.E.S.A.), London.

It is thought that the presence of from 10 to 20 per cent. free carbon in tar used for road work is desirable on account of its binding power and the resistance it lends to cracking of the surfaces ; moreover, there is a tendency to incorporate a certain proportion of bitumen, such as the varieties known as " Mexphalte " and " Shellphalte," both of which are derived from petroleum, and are soluble in carbon disulphide.

In addition to ordinary gas tar, other varieties include blast furnace tar and those which result from the distillation of wood, the production of water gas, the conversion of coal by hydrogenation into oil, and by the conversion of coal or its residues after carbonization into liquids by the action of catalysts on mixtures of carbon monoxide and hydrogen.

Analyses of Umea (pale Swedish pinewood tar) and dark pinewood tars, by A. Caroselli and C. Schneider, are given as follows :

	Umea Tar Per cent.	Dark Tar Per cent.
Water soluble acids calculated as acetic acid	1.1	2.88
Unsaponifiable constituents (aldehydes, ketones, alcohols, and hydrocarbons):		
(a) Volatile in steam	8.66	13.96
(b) Not volatile in steam	32.7	31.01
Constituents insoluble in sodium carbonate (phenols):		
(a) Volatile in steam	3.32	5.94
(b) Not volatile in steam	—	18.48
Constituents soluble in sodium carbonate (phenols):		
(a) Soluble in ether and estimated as acetates	13.38	—
(b) Insoluble in ether	—	10.0
Acids:		
(a) Insoluble in ligroin (hydroxy acids)	12.8	8.9
(b) Fatty acids estimated as ethyl esters	4.8	4.0
(c) Resin	16.5	2.5

and it is inferred that the resin content and the whole composition of the tars are largely dependent on the source and method of production, the resin content being a very important factor.

Beech-wood tar contains so-called lignoceric acid ( $C_{24}H_{48}O_2$ ), associated with a wax (lignocerin) which melts at  $79^\circ C.$ , and has been assigned the formula  $C_{48}H_{96}O_2$ .

*References:* *An Investigation into the Nature and Properties of Coal Tar*, by Evans and Pickard (South Metropolitan Gas Co., 1931); J. M. Weiss on "Distillation of Coal Tar (U.S.A. Practice)" (*Chem. and Ind.*, 51, 219, 246 (1932)); *Standard Methods for Testing Tar and its Products* (Standardization of Tar Products Committee, London; Heffer and Sons, Cambridge); Bunbury and Davidson on *Industrial Applications of Coal-Tar Products* (Ernest Benn, London); Coke-ovens, Stockholm Tar, Wood (Distillation), and other references given under the heading of Coal.

**TAR ACIDS** — A common designation for mixtures of phenol (carbolic acid) and cresols that are extracted by caustic soda (NaOH) from coal-tar distillates. The tar acids are recovered by acidifying the caustic soda extract. (See Carbolic Acid, Cresylic Acid, and Tar.)

**TAR SANDS** — See Asphalt, and Torbanites.

**TARAXACUM (Taraxacum Root, Dandelion Root)** — The dried or fresh root of *Taraxacum officinale*, collected in the autumn. It contains a bitter principle, taraxacin, together with resin and various sterols. The fresh root is used for the preparation of the juice. Taraxacum was formerly used in medicine.

**TARRAGON OIL**—The volatile oil distilled from leaves and branches of *Artemisia Dracunculus*, containing methyl chavicol, *p*-methoxycinnamic aldehyde and terpenes; sp. gr. 0.900 to 0.949 at 15° C.; opt. rot. +2° to +9° at 20° C.; ref. ind. 1.5161 to 1.5170 at 20° C.; soluble in alcohol and ether. Used as a flavouring agent in spices.

**TARTAR**—A name applied loosely to salts of tartaric acid, but more particularly to potassium bitartrate ( $\text{KHC}_4\text{H}_4\text{O}_6$ ) which is deposited from fermenting grape juice and wines on long keeping. This is known in commerce as "crude tartar" or "argol," and gives the white crystalline "cream of tartar" (when purified by being dissolved in water and recrystallized), which is used in medicine and in the dyeing and baking-powder industries. In admixture with varying proportions of saltpetre it is sometimes used in making the black and white fluxes which are used in metallurgical and assaying operations, and when pounded and mixed with chalk and alum it makes an excellent powder for polishing articles of silver. (See "The Manufacture of Cream of Tartar," by J. W. Black (*Ind. Chem.*, 15, 270 (1939)); Argol.)

**TARTAR EMETIC**—See Antimony (Oxides).

**TARTARIC ACID** ( $\text{COOH}(\text{CHOH})_2\text{COOH}$ ) occurs in nature (either in the free state or in combination with potassium and calcium as tartrates) in many vegetable juices such as tamarinds, gherkins, mulberries, pineapples, unripe beetroot, and more particularly in grape juice in combination as potassium bitartrate. A considerable industry is carried on in Sicily, Spain, and other wine-producing countries in the production of tartaric acid from the lees containing potassium bitartrate and calcium tartrate. It is readily prepared in a crystalline state from this mixture by treatment with lime or calcium carbonate, followed by decomposition of the resulting calcium tartrate with sulphuric acid. When argol is used as the source, this crude tartar can be dissolved in hydrochloric acid and the solution then nearly neutralized with milk of lime, which causes the deposition of calcium tartrate, leaving potassium tartrate in solution. The calcium tartrate, after some purification, is decomposed by dilute sulphuric acid, causing precipitations of calcium sulphate and leaving the tartaric acid in solution. After filtering out the calcium sulphate, the tartaric acid solution is concentrated to crystallization.

The world's production is estimated at some 20,000 metric tons a year, Spain producing about one-fourth of the total world's supply of raw acid material.

The common or *d*-tartaric acid found in nature is optically active, crystallizes in large prisms (as  $\text{C}_4\text{H}_6\text{O}_6 \cdot \text{H}_2\text{O}$ ), and is soluble in water. It fuses at 170° C.; is decomposed at 180° C.; is used in calico-printing as a solvent for the mordant, and finds applications in making effervescent beverages and in medicine.

Tartaric acid is known in four distinct modifications—namely, the dextro acid described above, the lævo acid of same melting point, racemic acid (optically inactive by external compensation, and re-

solvable into optically active acid), and an inactive form (optically and permanently inactive by internal compensation) of m.p.  $143^{\circ}\text{C}$ . (See Argol, Racemic Acid, Stereoisomerism, and Tartar.)

**TAURINE** ( $\text{CH}_2\text{NH}_2\cdot\text{CH}_2\text{SO}_2\text{OH}$ ) — A crystalline body soluble in hot water, found present in fæces, and easily obtained by the action of acids upon bile.

**TAUROCHOLIC ACID** ( $\text{C}_{26}\text{H}_{45}\text{O}_7\text{NS}$ ) — A constituent of bile which is decomposed by boiling with acids, yielding cholic acid ( $\text{C}_{24}\text{H}_{40}\text{O}_6$ ) and taurine ( $\text{C}_2\text{H}_7\text{O}_3\text{NS}$ ). (See Bile.)

**TAUTOMERISM** — See Isomerism.

**TAWING** — The dressing of skins, or tanning processes with solutions of mineral salts such as alum or those of chromium; used particularly in respect of glove and kid leathers. (See Tanning.)

**TEA** — The dried leaves of plants of the genus *Camellia*, N.O. Ternstroëmiaceæ, including the two varieties *Thea sinensis* (China tea) and *C. theifera* (Assam tea), which are largely cultivated in China, Japan, India, and Ceylon. Tea contains an essential oil (which gives aroma to it), an active principle named theine (caffeine) ( $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ), legumin, and tannin, in varying proportions according to the nature of the tea and other circumstances attending its production. The amount of caffeine varies between 2.57 and 4.89 per cent. in dry Ceylon tea, 3.86 and 4.89 per cent. in Indian tea, and from 2.42 to 3.78 per cent. in Chinese tea, the tannin between 12 and 15 per cent., and the essential oil from  $\frac{1}{2}$  to 1 per cent. The tannin extracted from tea, when pure, has been described as a white substance which oxidizes in the air to a brown syrup, and is soluble in water, alcohol, acetone, etc., but insoluble in chloroform, benzene, and carbon disulphide, having a composition agreeing with the formula  $\text{C}_{20}\text{H}_{20}\text{O}_9$ . The Indian and Ceylon teas contain more tannin than the Chinese tea.

Taken in moderation, tea is a useful stimulant.

**TEAK** (*Tectona grandis*, N.O. Verbenaceæ)—A valuable, hard, durable wood found in Central and S. India, Burma, and Siam. The African variety from the west coast comes from *Oldfieldia Africana*, but is not so good as the best-known sort.

**TEA-SEED OIL** is expressed from the seeds of *Thea sasanqua* (about 24 per cent.), and is a clear, straw-coloured or yellowish oil, without odour or taste, closely resembling olive oil, for which it can be used as an adulterant, but, owing to the presence of a poisonous saponin body, it has been condemned in its crude state as an edible oil. Although botanically related to the plant from which tea is prepared, the two are quite distinct. There are several varieties on the market, and the Sasanqua oil from *Thea sasanqua* has a sp. gr. of 0.916 to 0.919, sap. v. of about 193.4 to 194, i.v. of 88 to 90, and ref. ind. of 1.471. It is used respectively as an illuminant, for soap-making, as hair oil, and for lubrication, and, when purified, for edible use.

The *Thea japonica* yields Tsubaki oil, which is very similar to tea-seed oil.

China supplies the largest quantity of the oil, and Japan has a small production. The oil from India and French Indo-China is obtained from the *Cammellia drupifera*.

**TEA-TREE OIL** — From *Leptospermum citratum*, Australia.

**TECHNETIUM** (Tc) — Element number 43, probable atomic weight 99, discovered by C. Perrier and E. Segrè, in 1937. The name masurium has been used for this element, but technetium was accepted (1949) by the International Union of Chemistry. Technetium was the first synthetic element to be created, hence its name. It was formed originally from molybdenum by bombardment with deuterons, and later prepared in quantity from the fission products of the atomic pile, technetium 99 constituting 6 per cent. of the products. It can also be made by irradiation of molybdenum with neutrons whereupon the product molybdenum 99 decays to technetium 99. It has been prepared in the metallic state, and its compounds have been studied, the per-technetates are brightly coloured, reminding thus of the permanganates.

“**TEFLON**” (Du Pont) — Trade-mark for polytetrafluoroethylene resin. Possesses notable heat resistance, electrical properties, resistance to weathering, and inertness to chemicals.

**TELLURITE** — See Tellurium.

**TELLURIUM** (Te) and its Compounds — Atomic weight 127.61. See Elements for other data. Tellurium occurs naturally to some small extent in pure crystalline form of No. 3 system, but is, for the most part, met with in combination in some rare minerals including *tellurite* (tellurium dioxide,  $\text{TeO}_2$ ), *tetradymite* (bismuth telluride,  $\text{Bi}_2\text{Te}_3$ ), *sylvanite* ( $(\text{Ag}, \text{Au})\text{Te}_2$ ), and *melonite* ( $\text{NiTe}$ ). It is also said to exist in mineral forms associated with gold in Hungary and Transylvania.

Tellurium is a bright white metal of lustrous appearance, soluble in nitric and sulphuric acids and strong potassium hydroxide; a poor conductor of heat and electricity; boils at a dull red heat, giving off a golden yellow vapour, and, when heated in the air, burns with a blue flame, forming the dioxide ( $\text{TeO}_2$ ). In general properties tellurium resembles sulphur and selenium. The metal can be prepared from bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) by fusion with sodium carbonate and carbon followed by treatment of the resulting product with water; this gives a solution containing sodium telluride, and upon exposure to the air, metallic tellurium is deposited as a grey powder, which can be purified by distillation in a current of hydrogen. It is also obtained in a grey, brittle form by reduction of tellurium dioxide. It does not tarnish in moist air, and finds uses in the making of high-resistance alloys, in electrical equipment, and the ceramic industries. In combination with hydrogen it forms hydrogen telluride ( $\text{H}_2\text{Te}$ ), an offensive poisonous gas soluble in water, which is decomposed by heat and deposits metallic tellurium as a crystalline sublimate. Its value in hardening lead and reducing the corrosion of the latter when present

in small proportion (0.06 per cent. Te) is the subject of a paper by W. Singleton and B. Jones in *Chem. and Ind.*, **52**, 211 (1933). Tellurium exists in several allotropic forms, the most familiar ones being the stable medium-grey crystalline solid with a metallic lustre and the amorphous form. (See *Rarer Metals*, by J. DeMent and H. C. Dake (Chemical Publishing Co., Brooklyn, N.Y.).)

There are three **oxides** of tellurium, namely, the trioxide ( $\text{TeO}_3$ ), an orange coloured solid; the dioxide ( $\text{TeO}_2$ ), a white solid; and the monoxide ( $\text{TeO}$ ), a black solid. The **acids** are telluric ( $\text{H}_2\text{TeO}_4$ ), and tellurous ( $\text{H}_2\text{TeO}_3$ ), which are analogous to sulphuric and sulphurous acids, respectively.

Two **chlorides** of tellurium are known, namely, the tetrachloride ( $\text{TeCl}_4$ ), and the dichloride ( $\text{TeCl}_2$ ), and corresponding **bromides** ( $\text{TeBr}_4$  and  $\text{TeBr}_2$ ), and iodides ( $\text{TeI}_4$  and  $\text{TeI}_2$ ).

Tellurium derivatives of the aliphatic  $\beta$ -diketones are stated to be very active germicides.

**TEMPERATURES (Critical)** — See Matter.

**TEMPERATURES (Notable)** — See Heat.

**TEMPERATURES (Standard)** — See Heat.

**"TENAPOL"** — See Waxes.

**"1080"** — Sodium fluoroacetate, a very toxic rodenticide. (See *Science*, **102**, 232 (1945); and Rodenticides.)

**TENNANITE** — Mineral of composition ( $4\text{Cu}_2\text{S} \cdot \text{As}_2\text{S}_3$ ), of crystal system No. 1, and sp. gr. 4.5, occurring in some parts of the United States.

**TENORITE** — Mineral black copper oxide ( $\text{CuO}$ ), of sp. gr. 6.25, found in some parts of the United States.

**TENSILE STRENGTH** — See Strength (Tensile).

**TENSIMETER** — An appliance used in determining vapour pressures.

**"TEPP"** — See Tetraethyl Pyrophosphate.

**TERBIUM (Tb)** — Atomic weight, 159.2. See Elements for other data. Terbium is one of the rare-earth group of elements, and a member of the yttrium group of the same. It is found in *gadolinite*, *samarskite*, *euxonite*, and *monazite*.

Two **oxides** of terbium are known, namely, the trioxide ( $\text{Tb}_2\text{O}_3$ ), and the peroxide ( $\text{Tb}_2\text{O}_4$ ); also a **chloride** ( $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$ ), a **nitrate** ( $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), and a **sulphate** ( $\text{Tb}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ ). The salts are crystalline and hygroscopic.

**TEREBENE** — A commercial product prepared from American or French turpentine by heating moderately with several successive small quantities of strong sulphuric acid until its action on polarized light is quite destroyed, and then, after washing, submitting to distillation. It is a mixture of hydrocarbons, of which inactive camphene is one and dipentene another.

**TEREPHTHALIC ACID** ( $C_6H_4(COOH)_2$  (1, 4)) — An oxidation product of turpentine, para-toluic acid, and cymene, which sublimes unchanged and is nearly insoluble in water and alcohol.

**“TERGITOL”** — Trade-mark for wetting agents, penetrants, emulsifying agents, and cleaning compositions used for accelerating the penetration of liquids into solid materials, for wetting large areas, and for increasing the miscibility of dissimilar liquids.

**TERNE-PLATES** — See Tin.

**TERPENE HYDROCHLORIDE (Pinene hydrochloride)** ( $C_{10}H_{17}Cl$ ) — A white crystalline substance, made by treating pinene in petroleum solution at  $-70^\circ C.$ , with dry hydrochloric acid gas. Above  $-10^\circ C.$  it readily isomerizes into bornyl chloride, an intermediate in the industrial production of camphor from oil of turpentine. Neither of these compounds is a true hydrochloride, as no chloride ions are present in solution; the chlorine-carbon link is covalent, not electrovalent.

**TERPENES** — Unsaturated hydrocarbons occurring very widely distributed in the essential, or volatile, oils of plants, and in oleoresins and oleo-gum resins, such as colophony and myrrh respectively. Most terpenes are highly refractive liquids, volatile in steam, and having pleasant odours, although fairly readily oxidized to substances less pleasantly smelling. They are classified as follows:

(1) *Monocyclic diolefin terpenes* ( $C_{10}H_{16}$ ), such as limonene, phellandrene, and sylvestrene.

(2) *Dicyclic monoolefin terpenes* ( $C_{10}H_{16}$ ), such as pinene, camphene, and bornylene.

(3) *Sesquiterpenes* ( $C_{15}H_{24}$ ), such as zingiberene and cadinene.

The oxygenated derivatives of the terpenes are of even greater importance than the terpenes themselves, and include such well-known substances as camphor, menthol, terpineol, terpin hydrate, borneol, and carvone. (See *Organic Chemistry*, by Perkin and Kipping, Part III (W. and R. Chambers, London); and *The Terpenes*, by J. L. Simonsen (Cambridge University Press); Dipentene, Hydrocarbons, Limonene, Pinene, Sylvestrene, and Turpentine.)

**TERPIN HYDRATE** ( $C_{10}H_{20}O_2 \cdot H_2O$ ) — The so-called hydrate of terpin may be prepared by the action of nitric acid and alcohol on oil of turpentine. It forms colourless crystals with a slight aromatic odour, and sublimes at  $100^\circ C.$  When treated with dilute sulphuric acid it becomes converted to a mixture of the isomeric terpineols. It is used as an expectorant in cough medicines and as a mild antiseptic.

**TERPINENES** — Three isomeric monocyclic diolefin terpenes, namely, *alpha*  $\Delta$  1, 3; *beta*  $\Delta$  3, 8 (9); *gamma*  $\Delta$  1, 4 (limonene is, for reference,  $\Delta$  1, 8 (9)). The *alpha* and *gamma* forms are found together in many essential oils, such as cardamom oil, coriander oil, and manila-elemi oil. Mixtures of these same two terpinenes are obtained by the action of acids on such terpene hydrocarbons as pinene or dipentene, and on such terpene alcohols as terpineol, linalool, or terpin hydrate.

**TERPINEOL** ( $C_{10}H_{17}.OH$ ) — A liquid terpene alcohol, occurring naturally in several volatile oils and prepared from terpin hydrate by hydrolysis with a dilute mineral acid. It melts at  $38^{\circ}$  to  $40^{\circ}$  C. and boils at  $220^{\circ}$  C. ; soluble in alcohol and ether. It is used in the preparation of synthetic perfumes such as artificial lilac and lily, and as a plasticizer in alcohol and oil varnishes.

**TERPINOL and TERPINOL HYDRATE** — Synonyms for terpin and terpin hydrate (see same), respectively.

**TERRA ALBA** — This term is variously used commercially in respect of kaolin, gypsum, burnt alum, or magnesia, but should be reserved for kaolin.

**TERRA COTTA** — Baked earth or clay in varieties of buff, yellow, and red colour. Articles made of it can be cleaned with sodium hydrosulphite.

**"TERSAN"** (Du Pont) — Trade-mark for a fungicide based on tetramethylthiuram disulphide. Used for the prevention of brown patch in lawns.

**TESTOSTERONE** — The male hormone, namely,  $\Delta^4$ -androst-17-ol-3-one, first isolated from testicular tissue in 1935 and subsequently prepared by the oxidative degradation of cholesterol. It is a white, odourless, and tasteless crystalline powder ; insoluble in water ; soluble in alcohol ; m.p.  $151^{\circ}$  to  $156^{\circ}$  C. Sterile pellets of testosterone are used in medicine for administration by implantation in the tissues.

**Testosterone Propionate** — A white, odourless, tasteless crystalline powder, prepared by treating testosterone with propionic anhydride ; insoluble in water ; soluble in alcohol and in fixed oils ; m.p.  $118$ – $122^{\circ}$  C. It is used in medicine as a sterile solution in a suitable fixed oil for administration by intramuscular injection. For a discussion of the uses of testosterone in medicine, see W. O. Thompson, *J. Amer. Med. Ass.*, **132**, 185 (1946). (See Hormones, and Methyltestosterone.)

**TETRACAINE HYDROCHLORIDE** — See Amethocaine Hydrochloride.

**TETRACHLORETHANE (Acetylene Tetrachloride)** ( $CHCl_2.CHCl_2$ ) is a colourless, non-inflammable, poisonous liquid of sweet sickening odour, sp. gr. 1.600, b.p.  $146^{\circ}$  C. ; insoluble in water, but soluble in alcohol and ether, and prepared by one process from acetylene by the action of chlorine in presence of iron as a catalyst and subsequent distillation ; it yields trichlorethylene by the action of lime. Tetrachlorethane is a good solvent of fats, oils, resin, rubber, etc. ; does not attack metals ; and is used in making films, lacquered goods, and artificial silk. (See Solvents and Solvent Action.)

**TETRACHLORETHYLENE (Perchlorethylene, Carbon Dichloride, Carbon Bichloride)** ( $CCl_2 : CCl_2$ ) — A colourless liquid solvent of ethereal odour, sp. gr. 1.623 and b.p.  $121^{\circ}$  C. ; soluble in alcohol and ether, made by action of chlorine upon ethylene ; and is an important solvent. Trade-mark is "Perclene" (Du Pont). Used in textile cleaning, as a vapour degreasing solvent, as a vermifuge, and as a solvent for rubber, waxes, gums, paraffin, and tar. (See Solvents and Solvent Action.)

**TETRADYMITÉ** ( $\text{Bi}_2\text{Te}_3$ ) — Mineral bismuth telluride, sometimes occurring also in combination with bismuth sulphide (as  $2\text{Bi}_2\text{Te}_3 \cdot \text{Bi}_2\text{S}_3$ ), of crystal system No. 3, and sp. gr. 7.2. (See Bismuth.)

**TETRAETHYL LEAD** — See Motor Spirit.

**TETRAETHYL PYROPHOSPHATE** ("TEPP") ( $(\text{C}_2\text{H}_5)_4\text{P}_2\text{O}_7$ ) — A light straw-coloured mobile liquid, of sp. gr. 1.2, and decomposing when heated above  $135^\circ\text{C}$ . It is miscible with water, acetone, alcohol, and a number of other organic solvents, but not miscible with petroleum fractions. During World War II a highly effective insecticide called "Bladan" was produced in Germany which was supposed to have as its active ingredient hexaethyl tetraphosphate. More recent work, however, has indicated that the active ingredient is more probably tetraethyl pyrophosphate (sometimes designated as "TEPP"). This compound is toxic to mites, aphids, spiders, and certain other pests at low concentrations; it is also toxic to higher animals, however, and further research will be required to determine the best conditions for use under practical conditions. (See "Tetraethyl Pyrophosphate," by J. S. Harris (*Agr. Chemicals*, Oct. 1947); *Chemistry of Insecticides and Fungicides*, by D. E. H. Frear, 2nd ed., (D. Van Nostrand Co., New York); *Insecticides*, and "Parathion.")

**TETRAHEDRITE** (Grey Copper Ore) — See Copper.

**TETRAHYDROFURFURYL ALCOHOL**  $\left( \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2\text{OH}) \right) -$   
 $\left( \text{O} \right)$

A colourless liquid, of sp. gr. 1.051 and b.p.  $177^\circ\text{C}$ ., miscible with water, with ethyl alcohol, and with diethyl ether. The dicarboxylic acid esters are discussed by J. N. Borglin in *Ind. Eng. Chem.*, 28, 35 (1936).

"**TETRALIN**" (Tetrahydronaphthalene) ( $\text{C}_{10}\text{H}_{12}$ ) — An incompletely saturated hydrocarbon liquid of pungent odour produced by the partial hydrogenation of naphthalene in the presence of a catalyst at  $150^\circ\text{C}$ . It is used as a solvent of waxes, resins, rubber, naphthalene, etc., also for removing printer's ink from old paper, as a substitute for turpentine in varnish and polish making, and as a benzol wash oil from coal gas. It boils at  $210^\circ\text{C}$ ., is of sp. gr. 0.98, and has a flash-point of  $176^\circ\text{F}$ . As it dissolves 3 per cent. of its weight of sulphur at ordinary temperatures and 40 per cent. at  $100^\circ\text{C}$ ., it can be used for extracting sulphur from spent oxide as produced in gas purification, and as a solvent in the textile and soap industries.

There is an intermediate product between "Tetralin" and "Dekalin" known as "Tetralin-extra" (being a mixture of about 20 per cent. "Tetralin" and 80 per cent. "Dekalin"), which boils at  $190^\circ\text{C}$ ., has a flash-point of  $140^\circ\text{F}$ ., and a sp. gr. of 0.900. When used as a substitute for turpentine in paints, it is of importance to take care that the ingredients are quite free from manganese, as otherwise, it is stated, the white paints so made show a tendency to redden. (See "Dekalin," and Hydrogen (Hydrogenation).)

**TETRATHIONIC ACID** — See Sulphur.

**TETRYL (2, 4, 6-Trinitrophenylmethylnitramine, Tetranitromethylaniline)**

$\left( \begin{array}{c} (2, 4, 6) \text{ (NO}_2\text{)}_3\text{C}_6\text{H}_2\text{-N-CH}_3 \\ | \\ \text{NO}_2 \end{array} \right)$  — An explosive prepared by nitration of

dimethylaniline or phenylmethylnitrosamine. A yellow solid of m.p. 129°–130° C. Quite stable, but more sensitive to impact, shock, and friction than T.N.T. Used as a booster for high-explosive shells, and as a component of detonating caps for T.N.T.

**TEXTILES** — Excepting wool and cotton, adequate data with respect to many important properties of woven fabrics relative to humidity and temperature are wanting. The "Mullen" bursting test is employed in respect of tensile strength on strips and yarns, and shows that wool (ordinary and unshrinkable) and viscose give almost identical curves for moisture content; cotton and linen, being similar, having a corresponding value of about 7 per cent.; while "Celanese" is low, being only 6 per cent. at 70 per cent. relative humidity.

*References*: "Structure of Textile Fibres," by P. Larose (*Chem. and Ind.*, **52**, 303 (1933)); report of discussion on "Colloid Aspects of Textile Materials and Allied Topics" in *Chem. and Ind.*, **51**, 836 (1932); *Textile Analysis*, by S. R. and E. R. Trotman (C. Griffin and Co., London); *Textile Chemistry*, by F. J. Cooper (Methuen and Co., London); *Introduction to Textile Chemistry*, by H. Harper (Macmillan and Co., London and New York); *Dyeing of Textile Fibres*, by Horsfall and Lawrie (Ernest Benn, London); *Textiles on Test: The Wearing and Washing Properties of Fabrics and Garments*, by J. G. Williams (Chapman and Hall, London); *Fundamentals of Fibre Structure*, by W. T. Astbury; *Textile Fibres and Their Uses*, by B. R. Andrews; *Bleaching, Dyeing, and Chemical Technology of Textile Fibres*, by S. R. and E. R. Trotman; *Fabrics and How to Know Them*, by B. R. Andrews; also Bleaching, Cotton, Kier Boiling, Linen, Silk, Silk Substitutes, and Wool.

"**THALAZOLE**" — See Phthylsulphathiazole.

"**THALISTATIN**" — See Phthylsulphathiazole.

**THALLIUM (Tl) and its Compounds** — Atomic weight, 204.39. See Elements for other data. Thallium occurs to the extent of about 17 per cent. in *crookesite*, associated with copper and silver as selenides ( $\text{Cu}_2\text{Se}_4$ ,  $\text{TlSe}$ ,  $\text{Ag}_2\text{Se}$ ) (of crystal system No. 1); also in many varieties of iron and copper pyrites, so that it can be obtained from the dust resulting from the roasting of pyrites. In one reported case, 4 pounds of thallium was recovered from 1,500 tons of pyrites, the dust containing 0.25 per cent., equal to 1 part thallium per 1,000,000 parts of pyrites. It is obtained from the sulphate by immersing strips of zinc in the solution, when the thallium is deposited upon the zinc in the form of a spongy crystalline mass; also by treating thallium iodide with metallic sodium.

Thallium a soft, heavy metal, dissolves in nitric and sulphuric acids, makes a mark on paper as lead does, and has chemical properties in common with lead and the alkaline metals. The spectrum of thallium

is a bright green line, and its volatile salts, such as the chlorides, colour the Bunsen flame green. Inasmuch as it undergoes oxidation in the air it has to be preserved in water to keep its normal bluish-white lustre. It forms alloys with many metals. Of special interest are thallium-lead alloys because of their super-electrical conductivity below liquid air temperatures. None of the thallium alloys should be employed in the food industry because of their poisonous nature. (See article on "The Industrial Applications of Thallium and Its Compounds" in *Chem. and Ind.*, **52**, 687 (1933); and *Rarer Metals*, by J. DeMent and H. C. Dake (Chemical Publishing Co., Brooklyn, New York.))

There are two **oxides** of thallium, namely, thallos oxide ( $Tl_2O$ ), and thallic oxide ( $Tl_2O_3$ ), the latter being a dark reddish powder, insoluble in water, and formed when the metal is melted in presence of air.

**Thallos Hydroxide** ( $TlOH$ ) — Made by dissolving thallos oxide in water, or adding a solution of barium hydroxide to one of thallos sulphate, and concentrating the filtrate from the precipitated barium sulphate; it crystallizes in yellow needles, is alkaline, and soluble in water.

**Chlorides** — White, slightly soluble thallos chloride is formed when metallic thallium is heated in chlorine gas (when it burns), or by precipitation of a thallos solution with hydrochloric acid. Thallic chloride ( $TlCl_3$ ) (m.p.  $25^\circ C.$  for the anhydrous substance) is a colourless body obtained by passing chlorine through water containing thallos chloride in suspension, and concentration of the resulting solution, when it crystallizes out as  $TlCl_3 \cdot 4H_2O$ . This compound is used in the preparation of certain vermifugal compounds. Thallium sesquichloride ( $Tl_2Cl_3$ ) is a yellow solid.

Thallos (valence 1) compounds resemble the corresponding alkaline metal compounds, in that the hydroxide, the carbonate, and the sulphate are soluble, but the sulphide and chromate resemble those of lead in being insoluble. The halides are insoluble. Thallic (valence 3) nitrate, sulphate, and halides are soluble in water, and tend to hydrolyse more readily than the corresponding thallos compounds.

The compounds of thallium are poisonous, and as such are used as rat poison and insecticide, and they are also used as a depilatory.

**THEBAINE** — See Opium.

**THEELIN (Estrone)** — See Oestrone.

**THEINE** — See Caffeine, and Tea.

**THENARDITE** ( $Na_2SO_4$ ) — A mineral of crystal system No. 4, and sp. gr. 2.7. (See Sodium (Sulphate).)

**THÉNARD'S BLUE** — See Cobalt Blue.

**THEOBROMA SEED** — See Cacao.

**THEOBROMINE** ( $C_7H_8O_2N_4$ ) — A white, crystalline, poisonous purine base (3, 7-dimethyl-2, 6-dihydroxypurine), of bitter taste, and m.p.  $330^\circ\text{C}$ . in a sealed tube (sublimes at  $290^\circ\text{C}$ .). It is the active principle of cacao beans, and allied in chemical constitution to caffeine. The content of theobromine varies with different parts of the bean from about 1 to 1.7 per cent. of the shelled beans, or 2.2 to 3.9 per cent. of the dried fat-free material, while the germ, as separated commercially, contains about 2.1 per cent. It is insoluble in chloroform, and slightly soluble in water or alcohol. Unlike caffeine, but like theophylline, it forms a water-soluble sodium derivative and, is used in medicine as a diuretic. (See Cacao, and Purine.)

**THEOPHYLLINE** ( $C_7H_8O_2N_4, H_2O$ ) — A white, crystalline alkaloid, namely, 1,3-dimethylxanthine, obtained from the leaves of *Camelia sinensis* or prepared by synthesis; appreciably soluble in cold water; soluble in alcohol; sparingly soluble in ether; m.p.  $269^\circ$  to  $272^\circ\text{C}$ . It is related to caffeine but has little or no action on the heart but more marked diuretic properties.

**Theophylline and Sodium Acetate** — An equimolecular mixture of theophylline and sodium acetate, consisting of a white crystalline powder; soluble in water; insoluble in alcohol and ether. It is used in medicine as a diuretic. (See Aminophylline.)

**THERM** — The name given by the British Parliament to 100,000 British thermal heat units (B.Th.U.) as the basis of coal-gas prices. The therms used are ascertained by multiplying the number of cubic feet consumed by the declared calorific value of the gas. One B.Th.U. is the amount of heat required (absorbed) to raise 1 pound of water 1 degree Fahrenheit (at its temperature of maximum density, which is  $39^\circ\text{F}$ .) (See Heat, and Steam.)

**THERMAL DIFFUSION** — The method of separating uranium isotopes dependent upon the higher rate of movement at a given temperature for light-mass particles. A thermal differential is maintained between the centre and walls of a vertical tube through which the gas containing  $U^{238}\text{F}_6$  and  $U^{235}\text{F}_6$  is circulated to accomplish their separation.

**THERMAL DISSOCIATION** — A reversible chemical change brought about by heat. (See Dissociation.)

**THERMAL INSULATION** — See Heat Transfer, and Refrigeration.

**THERMAL UNIT** — See Therm, and Heat.

**" THERMIT " PROCESS** — When a mixture of metallic aluminium powder and ferric oxide is subjected to ignition by a fuse or otherwise, the whole mass (" Thermit ") becomes incandescent, the aluminium combining with the oxygen of the iron oxide, and setting free the molten iron, which forms a layer below ( $\text{Fe}_2\text{O}_3 + 2\text{Al} = \text{Al}_2\text{O}_3 + 2\text{Fe}$ ). The fuse may consist of a ribbon of magnesium terminating in a ball of barium peroxide and aluminium powder in contact with the mixture. The reaction is that of a system capable of undergoing a rapid exothermic chemical change without evolution of gaseous products.

The temperature realized by this reaction is estimated at about

3,500° C., and is high enough to melt all known metals. The process is used as a welding application for the repair of broken castings and shaftings frequently without the necessity of their being moved from their places. A mould is placed so as to receive a charge of the molten iron, the excess metal being afterwards cut away or otherwise removed. This process is also used for making carbon-free metals and various alloys, including ferro-chrome, metallic chromium, metallic manganese, manganese-copper, manganese-zinc, and ferro-titanium; it is also applied in making incendiary bombs.

The method may be used for the reduction of difficultly reducible oxides to their corresponding metal, such as tungsten oxide to tungsten.

**THERMOCHEMISTRY** deals with the thermal changes involved in chemical interactions. (See Chemical Interactions, and Heat (Thermochemical Aspects).)

**THERMOCOMPRESSION** — See Evaporation.

**THERMODYNAMICS** — The study of the relationships between heat and work. (See Energy.)

**THERMO-ELECTROMOTIVE FORCE** — That arising from a temperature difference at the junction of two metals, as employed in a thermopile. (See Electricity, and Pyrometers.)

**THERMOMETERS** — Instruments used to register and measure the intensity of heat, that is, temperature, are called thermometers. There are four fundamental types of thermometers that operate upon different physical principles.

The first type is the expansion-type thermometer that contains some fluid (like mercury) that expands as heat is applied and contracts as heat is removed. By proper choice of fluid and container this type of thermometer can cover a fairly wide range of temperatures, and it is easy and convenient to use. For example, the ordinary mercury thermometer can measure temperatures between  $-40^{\circ}\text{C.}$  and  $+360^{\circ}\text{C.}$ ; an 8.5 per cent. thallium-mercury amalgam to  $-60^{\circ}\text{C.}$ ; toluene to  $-100^{\circ}\text{C.}$ ; liquid pentane to liquid air temperatures (about  $-200^{\circ}\text{C.}$ ); gallium in quartz to  $+1,000^{\circ}\text{C.}$

Gas thermometers can cover large temperature ranges but are very inconvenient to use except as ultimate standards. The hydrogen constant-volume thermometer is the standard on which the Centigrade and Absolute temperature scales are based, but due to the fact it is so inconvenient to use the Seventh General Conference on Weights and Measures in 1927 established the international temperature scale as a reliable secondary standard for general use (see Heat (Temperatures)).

The second type is based upon the principle that the electrical resistance of a wire increases in a regular manner as the temperature rises. Since the electrical resistance of a wire can be measured with great precision by a Wheatstone bridge this method becomes a very accurate method for determining temperature. Usually high-grade

platinum wire is used for this purpose and special apparatus is required when very precise work is being done. Under proper conditions temperature can be measured with a precision of  $\pm 0.001^\circ \text{C}$ . with this type of instrument. The range is between  $-200^\circ \text{C}$ . and  $+660^\circ \text{C}$ .

The third type is the thermopile or thermocouple, where an electric current is produced in a closed circuit of two different metals whose two junctions are at different temperatures (see Pyrometers). Temperature range  $-200^\circ \text{C}$ . to  $1,450^\circ \text{C}$ .

The fourth type, the optical pyrometer, operates upon the principle that the kind of radiation emitted by a hot body is related to the temperature of emitter. The intensity of the radiation from the carbon filament energized by a variable-resistance electrical system is matched to that of the unknown object by adjusting the amount of current through the carbon filament. The amount of current necessary to make the carbon filament match the furnace radiation is related to the temperature by tables which go with the optical pyrometer. By using filters with known factors the actual temperature of the furnace may be many times that of the carbon filament, yet the temperature can be determined from tables. These instruments are very easy to use, and popular in industry. They are not suitable for temperatures below  $1,000^\circ \text{C}$ .

**THERMOPILE (Thermo-Couple)** — See Pyrometers, and Thermometers.

**THERMOSTATS** — Apparatus designed to maintain a constant temperature based upon the unequal expansion of different metals, liquids, or gases by the agency of heat. The simplest form is that of a water-bath heated by a gas lamp, together with a device for automatically controlling the supply of gas to the burner, so that the temperature of the water is kept constant. A simple electrically controlled thermostat is described by J. A. Cranston (*J.C.S.*, 1930, 1459); one for use in corrosion research by U. R. Evans (*Chem. and Ind.*, 50, 66 (1931)).

**THIAMIN** — See Vitamins.

**THIAZOLE**  $\left( \begin{array}{c} \text{CH} : \text{CH} : \text{N} : \text{CH} \\ | \quad \text{---} \text{S} \quad \text{---} | \end{array} \right)$  — An organic colourless liquid, of b.p.

$117^\circ \text{C}$ ., and an odour resembling that of pyridine. It is less basic than pyridine. Derivatives of thiazole are of great importance in medicine, *e.g.*, sulphathiazole.

**THINNERS** — See Paints.

**THIO** — A prefix used in respect of certain compounds in which oxygen is replaced by sulphur, as in thioalcohols, and in thiosulphates.

**THIOACETALS** — Sulphur compounds analogous to the acetals, such as acetone ethyl mercaptol  $((\text{CH}_3)_2\text{C}(\text{S.C}_2\text{H}_5)_2)$ .

**THIOACIDS (Sulpho-Acids)** — See Sulphur.

**THIOALCOHOLS** — See Mercaptans.

**THIOCARBAMIDE** — See Thiourea.

**THIOCARBANILIDE (Diphenyl Thiourea)**  $((C_6H_5NH)_2CS)$  — A colourless crystalline substance prepared by interaction of carbon disulphide and aniline; of m.p.  $154^\circ C.$ ; soluble in alcohol and ether. Used in organic syntheses, and as a flotation reagent.

**THIOCARBONYL CHLORIDE (Thiophosgene)**  $(CSCl_2)$  — Prepared by the action of chlorine on carbon disulphide followed by steam distillation; a red, mobile, fuming liquid of b.p.  $73.5^\circ C.$ , and of irritating odour, and resembling phosgene in chemical characters; used in the dyestuffs industry.

**THIOCOLL (Potassium Guaiacol-3-Sulphonate)**  $(C_6H_3(OH)(OCH_3)SO_3K)$  — Used in medicine for same applications as guaiacol, being less irritant.

**THIOCYANATES (Sulphocyanides)** are combinations of bases with thiocyanic acid  $(HCNS)$ . By fusion of sulphur with potassium cyanide or sodium cyanide the corresponding potassium thiocyanate  $(KCNS)$  and sodium thiocyanate  $(NaCNS)$  are formed. They are readily soluble in water, are not poisonous, and are used in the textile trade, in black nickel-plating, photography, dyeing, and calico-printing.

Mercury thiocyanate is used in making so-called "Pharaoh's serpents," owing to the fact that when heated it swells, grows in fantastic form to great size, and retains the resulting formation.

Thiocyanates result from the action of free thiocyanogen upon various metals, and can be prepared from the ammoniacal liquor of gasworks. (See Gas (Coal).)

**THIOCYANOGEN**  $((SCN)_2)$  is a viscid, unstable, yellow oil, obtained by action of bromine dissolved in carbon disulphide, or carbon tetrachloride solution, upon a metallic thiocyanate, such as silver, lead, or mercury, and evaporation of the solution *in vacuo*:  $2MSCN + Br_2 = 2MBr + (SCN)_2$ . When a solution of thiocyanogen in carbon disulphide is cooled to  $-70^\circ C.$ , the body is stated to separate in crystalline form. It can also be produced by the electrolysis of alkali thiocyanates in aqueous or alcoholic solution. It yields organic thiocyanates by combination with such groups as methyl, and has been advocated for use in volumetric analysis, a solution in acetic acid having been employed for "rhodanometric" determinations of the iodine values of fats and oils.

**THIOGLYCEROL**  $(CH_2SH.CHOH.CH_2OH)$  — A sulphohydryl compound that promotes the healing of obstinate wounds, ulcers, and sores, and is useful in skin-grafting. One part in 5,000 is used in glycerol, water, or physiological salt solution.

**THIOGLYCOLLIC ACID**  $(HS.CH_2COOH)$  — The sulphur analogue of glycollic acid. The ammonium salt is used in permanent-waving solutions and in the popular "home-perm" kits.

**"THIOKOL"** — An oil-resistant, rubber-like material made by the reaction of polysulphides with ethylene dichloride or dichloroethyl ether compounds. The resistance is notable to hydrocarbons, acids, and mild alkalis. (See Rubber.)

**THIOUREA (Thiocarbamide)**  $((\text{H}_2\text{N})_2\text{CS})$ —A white, crystalline compound prepared by heating dry ammonium thiocyanate at  $130^\circ\text{C}.$ ; soluble in water and in alcohol; m.p.  $180^\circ$  to  $182^\circ\text{C}.$  It may also be prepared by the action of hydrogen sulphide on cyanamide,  $\text{CN.NH}_2$ . It has the pharmacological action of inhibiting the synthesis of thyroid hormone and has been used in medicine for the treatment of thyrotoxicosis, but has been replaced by thiouracil and methylthiouracil which have lower toxicity (see W. R. Trotter, *J. Pharm. and Pharmacol.*, **2**, 65 (1949)). It is also used in photography and in the manufacture of "Beatl" resin.

**THIRAM** (Tetramethylthiuram Disulphide) — A fungicide.

**THOMSONITE** — One of a series of minerals (crystal system No. 4, and sp. gr. about 2.3) which may be viewed as mixed crystals of the end members  $\text{CaO}, \text{Al}_2\text{O}_3, 2\text{SiO}_2, 3\text{H}_2\text{O}$  (calcio-thomsonite) and natrolite.

**THORIANITE** — A heavy black mineral containing a large proportion of thorium ( $\text{ThO}_2$ ) mixed with uranium oxides, etc., found in Ceylon and Montana. It usually occurs in small cubes, and has a sp. gr. of 9.5.

**THORITE** — A mineral consisting essentially of silicate of thorium, yellow to dark brown in colour, of crystal system No. 2, and sp. gr. 4.4 to 5.4; found in Ceylon and Norway.

**THORIUM** (Th) and its Compounds — Atomic weight, 232.12. See Elements for other data. Thorium is a rare metal occurring in the minerals *carnotite*, *thorite*, *thorianite*, *orangite*, and *monazite*. In the form of oxide (as obtained from the nitrate by heating, and fusible at a temperature of about  $2,800^\circ\text{C}$ .) it is used in the preparation of incandescent gas mantles. The purer thorium compounds are obtained from monazite sand, which is essentially a phosphate of the cerium earths and occurs naturally in extensive deposits in Carolina, the coast of Brazil, and Travancore. The separated monazite from the Travancore deposits contains about  $8\frac{1}{2}$  per cent. of thorium, as compared with 6 per cent. in the best concentrates from the Brazilian sands. The process of its extraction from ores and other particulars are given in an article by C. M. Dyson (*Ind. Chem.*, 7, 231 (1931)).

Thorium can be obtained by heating the double chloride of thorium and potassium with metallic sodium, and as thus produced is a grey, dense, almost infusible powder. Another procedure is that proposed by J. W. Marden (*Trans. Electrochem. Soc.*, 66, 39 (1934)) in which equal weights of potassium and sodium chloride are fused with potassium thorium fluoride and electrolysed with a molybdenum cathode in a graphite crucible.

Pure thorium is ductile and can be drawn into wire and when heated in air it burns with great brilliancy. The metal is readily dissolved in nitric acid and to a lesser extent in dilute sulphuric and hydrochloric acids. It forms alloys with various metals. By adding 0.75 per cent. thorium to tungsten filament wire, superior electron-emission quality results. Thorium is not subject to nuclear fission when bombarded with slow neutrons but may conceivably compete with uranium as a source of atomic power by conversion into uranium-233 in much the same way as plutonium is made from ordinary uranium. (See *Rarer Metals*, by J. DeMent and H. C. Dake (Chemical Publishing Co., Brooklyn, N.Y.).)

Two oxides of thorium are known, namely, the dioxide ( $\text{ThO}_2$ ), sometimes used as a promoter with nickel catalysts, and is the principal component of the white ash of Welsbach gas mantles; and the peroxide ( $\text{Th}_2\text{O}_7$ ). Both oxides are insoluble in water.

The important salts of thorium are the **nitrate** ( $\text{Th}(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$ ), very soluble in water; the **sulphate** ( $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$ ), very slightly soluble in water; and the **chloride** ( $\text{ThCl}_4$ ), very soluble in water.

Mesothorium (see Radioactivity) exhibits properties similar to those of radium, for which it is used as a substitute. It is a regular by-product of the manufacture of gas mantles from monazite sand, is employed medicinally, and is specially adapted for making luminous paint by admixture with zinc sulphide, particularly in respect of articles required for comparatively short periods. (See Gas Mantles, and Monazite.)

**THUJA OIL** — A pale yellow, volatile oil, of agreeable odour, distilled from the leaves of the white cedar, *Thuja occidentalis*; it contains thujone, *l*-fenchone, and pinene; soluble in alcohol and ether; sp. gr. 0.915 to 0.925 at 15° C.

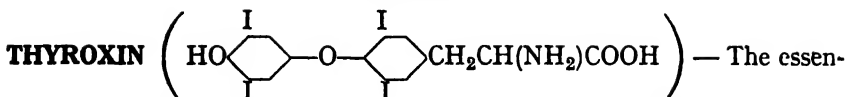
**THULIUM** (Tm) — Atomic weight 169.4. See Elements for other data. Thulium is an element of the rare-earth group and belongs to the yttrium group of the same, found in association with yttria in a number of minerals, including *gadolinite*, *keilhauite*, *euxenite*, and *samarskite*.

**THYME OIL** — A volatile oil obtained by distillation from the leaves and flowering tops of *Thymus vulgaris* and other species of *Thymus* (Fam. Labiatæ). It contains from 40 to 45 per cent. of phenols, consisting of thymol and carvacrol; soluble in alcohol and ether; sp. gr. 0.905 to 0.960 at 15° C.; opt. rot. 0° to +4° at 20° C.; ref. ind. 1.483 to 1.510 at 20° C. The oils richest in phenols (up to 67 per cent.) are distilled from the Andalusian *Thymus Zygis* and *Corydorthymus capitatus*. Thyme oil is used in liniments for its rubefacient and counter-irritant properties. (See Thymol.)

**THYMOL** (C<sub>10</sub>H<sub>13</sub>OH) — A colourless, crystalline compound, namely, 1-methyl-4-isopropyl-3-methylbenzene, obtained from origanum, monarda, or ajowan oils, or prepared synthetically; very sparingly soluble in water; soluble in alcohol and chloroform; m.p. about 50° C.; b.p. 232° C. It can be synthesized by hydrogenation of piperitone obtained from *Eucalyptus dives* and *E. piperita*; another synthesis depends upon the nitration of *p*-cymene, reduction with aluminium amalgam, diazotization, and treatment with stannous chloride. Thymol is used in medicine for the treatment of hook-worm and as an antiseptic.

The thymol content of various volatile oils has been reported as follows:

Ajowan oil	..	..	..	..	..	40 to 50%
<i>Thymus vulgaris</i>	..	..	..	..	..	20 to 30%
<i>Monarda punctata</i>	..	..	..	..	..	60%
<i>Carum copticum</i>	..	..	..	..	..	45 to 55%
<i>Ocimum viride</i>	..	..	..	..	..	37%
<i>Origanum hirtum</i> (from Crete and Dalmatia)	..	..	..	..	..	60 to 67%
<i>Mosla japonica</i>	..	..	..	..	..	44%
Wild thyme of France	..	..	..	..	..	20%



tial hormone constituent of the thyroid gland, being an iodine compound used in medicine. It has been isolated in a crystalline state, it is produced by the thyroid gland and is a precursor of the thyroid hormone which is essential for normal growth and development of the body. Deficiency of the thyroid hormone results in cretinism in children and myxœdema in the adult. These conditions can be treated by the administration of thyroxine, but dried thyroid gland extracts are usually used in medicine for these conditions. It was first isolated from the thyroid gland by Kendall, and first synthesized by C. R. Harington. It is manufactured by a number of steps from quinol and *para*-nitroaniline. (See *Thyroxine*, by E. C. Kendall (Reinhold Publishing Co., New York); and recent developments, J. Elks and B. A. Hems in *Pharm. J.*, **109**, 508 (1949).)

**“TIMONOX”** — A proprietary brand of a white oxide of antimony, claimed to possess the essential requirements of a first-class pigment, having good oil absorption, good covering power, great opacity, perfect freedom from crystals, and easily ground with oil. It is also used in the enamel industry as an opacifier.

**TIN (Sn) and its Compounds** — Atomic weight 118.70. See Elements for other data. Tin is found in nature for the most part in the form of oxide ( $\text{SnO}_2$ ) in the mineral known as *tin-stone* (*cassiterite*) in Cornwall, the production in that county in 1890 amounting to 15,000 tons, but only to 6,000 tons in 1918; it also occurs in Australia, Bolivia, Burma, Canada, Nigeria, and Mexico, but the Malay States is the chief producer. The metal is ordinarily prepared—after washing the gravel containing the ore—by calcination, whereby the associated sulphur and arsenic are burnt off as sulphur dioxide and arsenious oxide, and any metallic iron and copper are oxidized. The residue is washed, thereby dissolving any copper sulphate produced in the calcination, and the lighter associated matters including the iron oxide are removed. The heavier purified ore is then reduced by smelting with coal in a reverberatory furnace ( $\text{SnO}_2 + 2\text{C} = \text{Sn} + 2\text{CO}$ ), and the resulting metal further purified by heating in another furnace with green wood until the tin melts and flows away from associated alloys and the dross. The solidified product is known as “block tin.” (See *Tin: its Mining, Production, Technology, and Applications*, by C. L. Mantell (Reinhold Publishing Corp., New York).)

“Chempur Tin” is a specially refined Straits Settlements product, said to contain less than one-twelfth of the impurities ordinarily occurring in the “Straits” tin.

Tin is a bright white metal obtainable in crystalline form, and does not tarnish in the air; is fairly soft, ductile, of poor electric conductivity, and malleable, but at 228° C. it becomes quite brittle. So-called “grey tin,” resulting from exposure of the white metal to a temperature below

18° C., has a sp. gr. of 5·8, and is an allotropic form and is reconverted into the white form, of sp. gr. 7·3, on raising the temperature to above 18° C. A very small percentage of aluminium is sufficient to make tinfoil brittle in a short time.

### TIN AND TIN ORE, WORLD PRODUCTION

Annual average for the three-year period 1937–1939.

Data arranged and rounded off by the Editor.

Country				Tin Metric Tons		Tin Ore (Sn content) Metric Tons
United Kingdom	..	..	..	32,000		2,000
Netherlands	..	..	..	23,000		
Belgium	..	..	..	5,000		
Germany	..	..	..	4,000		
Portugal	..	..	..	1,000		
				<hr/>	65,000	
Bolivia	..	..	..			26,000
Argentina	..	..	..			2,000
Malaya	..	..	..	80,000		58,000
Netherlands Indies	..	..	..	12,000		31,000
China	..	..	..	11,000		12,000
				<hr/>	103,000	
Burma	..	..	..			6,000
Thailand	..	..	..			16,000
Japan	..	..	..			2,000
Belgian Congo	..	..	..	2,000		9,000
				<hr/>	2,000	
Nigeria	..	..	..			10,000
Australia..	..	..	..	3,000		3,000
				<hr/>	3,000	
Sum of above	..	..	..		173,000	177,000
WORLD PRODUCTION	..	..	..		179,000	181,000

Many chemical methods have been advocated and used for the recovery of tin from waste materials, including the use of chlorine in carbon tetrachloride and subsequent distillation of the solvent from any stannic chloride thus obtained; others for dissolving the tin and extraction of the metal from the resulting solution by treatment with an aluminium or zinc alloy; and many electrolytic processes, the general principle involved being the electrolysis of the metallic waste products in an alkaline or acid solution.

The metal dissolves in cold dilute nitric acid, stannous nitrate

being formed, and in concentrated hydrochloric acid to form stannous chloride, but forms insoluble white metastannic acid with concentrated nitric acid.

Tin is largely used in the process of tinning iron and other metals and making metal joints. Ordinary tinplate consists of very mild steel containing about 0.1 per cent. carbon, coated with tin on the surface by dipping into a bath of the molten metal. The plates are first of all "black pickled" by moving them about in hot, weak (7 per cent.) sulphuric acid to remove oxide scale, washed, then piled up wet for "black annealing," a process in which they are heated for ten to twelve hours in a furnace with a reducing flame. After being rolled (during which they become hardened), they are "white pickled" in a weaker bath of acid. Finally, they are passed through a strong solution of zinc chloride (which is used as a flux) and then into the molten tin. In its final stage the tinplate is passed through a bath of boiling hot palm oil. A variety of tinplates of inferior character known as "terneplates" are coated with lead or with an alloy of tin and lead of varying composition, such as, 1 lead and 2 tin or 2 lead and 1 tin.

According to Sir T. Legge's account of the process of tinning hollow ware, iron articles are cleaned by immersion in a tank of hot dilute hydrochloric acid, then dipped into a cold weak acid solution of zinc chloride, and subsequently immersed in a molten bath of 40 per cent. tin and 60 per cent. lead, the excess of metal on the articles being afterwards wiped off, using a pad of tow held by the worker's hand for that purpose. The cases of poisoning to which this process gives rise are due to escaping vapours of the chlorides of lead, zinc, and tin into the air. Methods of avoiding such poisoning are also dealt with in Legge's lecture (published by the Institute of Chemistry, 1930).

"Chemical tinning" is effected by immersion of the subject articles in a solution compounded of cream of tartar, ammonium alum, and stannous chloride at about 180° to 190° F. "Cold tinning" is carried out by cleaning the article with strong hydrochloric acid, application of a soft amalgam of tin, and distilling off the mercury by heat.

Electroplating has the advantage over hot-dip plating of high-speed production and the saving of one-half to one-third in tin consumption. One steel mill reported processing electro-tin plate at a rate exceeding 1,000 feet per minute. (See *Steel*, 114 (Feb. 7, 1944); *Metal Finishing*, 42, 77 (Feb., 1944); *Tinplate*, by W. E. Hoare and E. S. Hedges (Edward Arnold and Co., London).)

Pure tin has valuable applications by reason of the fact that it is innocuous when used for the preservation of foods and is not acted upon by many chemicals which attack iron and some other metals. Tin cans, wrapping foil, and collapsible tubes have been extensively employed for this purpose. In alloys tin is used in solders, babbitt, and other antifriction metals; for bronzes and other alloys, such as Britannia metal, "Magnolia," and pewter; and in die castings. Almost all the so-called "white metals" contain tin as an alloy. (See *Tin Solders*, by S. J. Nightingale and O. F. Hudson (British Non-Ferrous Metals Research Association, London); and *Metals*

Vol. II, by H. Carpenter and J. M. Robertson (Oxford University Press, London.)

The analysis of the British chemical standard tin-base white metal B is as follows: tin, 84.0 per cent.; antimony, 7.52 per cent.; copper, 4.03 per cent.; lead, 3.86 per cent.; zinc, 0.40 per cent.; iron, 0.05 per cent.; and arsenic, 0.04 per cent.

**Oxides** — When strongly heated in the air, tin takes fire and forms stannic oxide ( $\text{SnO}_2$ ), a white, insoluble, amorphous substance which turns yellow on heating, is not acted upon by acids or alkalis, and is used in making "putty powder"; also as a polishing-powder for steel and glass, and in the manufacture of certain kinds of glass. The stannous oxide ( $\text{SnO}$ ) can be prepared by heating the oxalate out of contact with air, or in hydrated form ( $3\text{SnO} \cdot 2\text{H}_2\text{O}$ ) by adding a solution of sodium carbonate to one of stannous chloride. It is soluble in acids, forming stannous salts, and when heated in the air it becomes oxidized to stannic oxide. The hydroxide dissolved in sodium hydroxide is used by calico printers under the name of "sodium stannite."

**Stannic Acid** ( $\text{H}_2\text{SnO}_3$ ) is obtained in hydrated form by adding a solution of sodium carbonate to one of stannic chloride in insufficient quantity for complete precipitation, and, as thus produced, is a white gelatinous body insoluble in water, forming, with excess of sodium hydroxide solution, sodium stannate, which is soluble in water, and used as a mordant under the name of "tin preparing salt" ( $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ ). It is made by fusing metastannic acid with sodium hydroxide.

**Metastannic Acid** ( $\text{H}_{10}\text{Sn}_5\text{O}_{15}$ ) — A white powder obtained by the action of strong nitric acid upon tin.

**Stannous Chloride** ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ), a white, crystalline body, soluble in water, obtained by dissolving tin in concentrated hydrochloric acid; used in ink-making, also as so-called "tin salts" and "tin crystals" by calico printers and dyers and in tin galvanizing. It can be obtained in the anhydrous state by treatment with acetic anhydride.

**Stannous Chromate** ( $\text{SnCrO}_4$ ) — A brown substance, insoluble in water, used in decorating porcelain.

**Stannous Sulphate** ( $\text{SnSO}_4$ ) — A heavy, white, crystalline powder, soluble in water, used in dyeing and electroplating. According to Mathers and Rothrock, 15 parts of tinfoil or of electro-deposited tin in a spongy condition dissolves readily in 40 parts of 75 per cent. sulphuric acid with a final temperature of  $140^\circ \text{C}.$ , yielding stannous sulphate free from stannic sulphate.

**Stannous Oxalate** ( $\text{SnC}_2\text{O}_4$ ) — A heavy, white, crystalline powder, obtained by the action of oxalic acid upon tin, or stannous oxide; soluble in acids, and used in dyeing and printing textiles. When heated without free access of air, it forms black stannous oxide.

**Stannous Sulphide** ( $\text{SnS}$ ) — A leaden-coloured substance formed when tinfoil is introduced into the vapour of sulphur, the metal taking fire in the reaction. In hydrated form it is produced by passage of hydrogen sulphide gas into a stannous solution.

**Stannous Tartrate** ( $\text{SnC}_4\text{H}_4\text{O}_6$ ) is a heavy, white, crystalline substance, soluble in water, used in the textile industries.

**Stannic Chloride** ( $\text{SnCl}_4$ ) is obtained by the action of chlorine gas on the metal, also by passing chlorine in excess through a solution of stannous chloride. In the pure anhydrous state it is a colourless liquid which boils at  $114^\circ \text{C.}$ , fumes in the air, and forms several hydrates with water. Of these  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  is crystalline, soluble in water, and is used as a mordant; but for that purpose it is more usually prepared by dissolving tin in cold aqua regia, when it is commercially known as "oxymuriate of tin." The salt is used also for weighting silk, in tinning of vessels, etc.

**Stannic Chromate** ( $\text{Sn}(\text{CrO}_4)_2$ ) is brown, soluble in water, and used in decorating porcelain.

**Stannic Sulphide** ( $\text{SnS}_2$ ) is a bright yellow crystalline powder used as a pigment for imitation-gilding under the name of "mosaic gold," and is obtained as the result of complicated changes by heating tin amalgam together with sulphur and ammonium chloride. It is soluble in alkaline sulphide solutions, and can be sublimed to some extent. (For details concerning the preparation and applications of mosaic gold see Hans Hadert, *C.T.J.*, **78**, 32 (1926).)

**Stannic Phosphide** ( $\text{Sn}_2\text{P}_2$ ), a silver-white compound made by heating the metal with phosphorus; used in making phosphor-bronze.

There are numerous organic compounds of tetravalent tin, more than 150 of these having been described. Tin tetraethyl is a colourless liquid, of b.p.  $181^\circ \text{C.}$  (See also Purple of Cassius.)

**TIN CRYSTALS** — See Tin (Stannous Chloride).

**TIN PREPARING SALT** — See Tin (Stannic Acid).

**TINCAL (Tinkal)** — See Boron.

**TINCTURES** — Alcoholic preparations, usually prepared from vegetable drugs either by extraction of the crude drug or by dilution of a liquid extract. (See Extracts.)

**TINPLATE** — See Tin.

**TIN-STONE** — See Tin.

**TINTOMETERS** — See Colorimeters.

**TITANITE** ( $\text{CaO}, \text{TiO}_2, \text{SiO}_2$ ) — A mineral of crystal system No. 5, and sp. gr. about 3.5. (See Titanium.)

**TITANIUM (Ti) and its Compounds** — Atomic weight 47.90. See Elements for other data. This element occurs plentifully in several mineral forms: as oxide ( $\text{TiO}_2$ ) in *anastase*, *brookite*, and *rutile*, and in other forms in *ilmenite*, *titanite*, and *titano-columbates*, although there are no large deposits in Great Britain. It is also found present in Nile silt, and finds some employment in metallurgy. Deposits of *rutile* exist in Norway, U.S.A., Tasmania, and Australia, and are marketed in the form of black concentrates containing from 93 to 98 per cent. Titaniferous iron-ore is found in quantity in the Adirondack Mountains of North-Eastern United States. Their development depended upon the work of A. J. Rossi, and the interesting story appears in the report of the Perkin Medal Award to Rossi (*Ind. Eng. Chem.*, **10**, 138 (1918)).

Rutile and ilmenite ( $\text{FeTiO}_3$ ) are found in Eastern Canada, New York, Virginia, North Carolina, and Florida. Ilmenite also occurs in Tasmania and Madagascar, but the largest deposits occur in Quebec and Norway. A deposit associated with uranium exists at Olary in South Australia, and is used as a source of radium and titanium oxide.

Ilmenite, containing from about 34 to 44 per cent.  $\text{TiO}_2$ , is chiefly used in the manufacture of ferro-titanium alloys, arc-lamp electrodes, and titanium oxide pigment; while rutile is chiefly used in the preparation of titanium compounds and sometimes to give a yellow colour to porcelain.

### TITANIUM CONCENTRATES, WORLD PRODUCTION

Annual averages for the two-year periods, namely, 1938-1939 and 1943-1944

Data arranged and rounded off by the Editor.

Country	Metric Tons			
	Ilmenite (45 to 55% $\text{TiO}_2$ )		Rutile (88 to 94% $\text{TiO}_2$ )	
	1938-39	1943-44	1938-39	1943-44
Norway .. ..	52,000	?	100	100*
Portugal .. ..	500	100*	—	—
Spain .. .. .	—	400	—	—
U.S.A. .. .. .	13,000*	219,000	?	5,000
Canada .. .. .	1,800	47,000	—	—
Brazil .. .. .	100	3,000*	400	3,000
British India .. ..	260,000*	38,000*	—	—
Malaya .. .. .	8,800	?	—	—
French Cameroons ..	—	—	100	2,900
Senegal .. .. .	6,000	700*	—	—
Australia .. ..	—	6,500	600	7,700

\* Estimated

Titanium is a silver-white metal, one-half the density of iron and less than twice the density of aluminium; as hard as iron; as strong as stainless steel and stronger than aluminium; resists corrosion (especially well against salt water) about the same as stainless steel; and has a high melting point ( $1,820^\circ\text{C}$ ). It is used in metallurgy, alloyed with other metals, for a number of purposes, ferro-titanium

alloys being used as deoxidizing agents, and as oxygen and nitrogen scavengers, a small quantity of titanium (which readily forms nitride) being of advantage for the final purification of nearly all grades of steel, while cupro-titanium and mangano-titanium alloys are used in brass and bronze practice. It is stated that mercury ceases to attack iron at high temperature and high pressure if one part per million of titanium is added.

The first pure titanium metal that is malleable when cold was produced by M. A. Hunter (*J. Amer. Chem. Soc.*, **32**, 330 (1910)). The metal is brittle when contaminated with impurities or upon reaction with such gases as hydrogen, oxygen, and nitrogen. The most practical process for the large-scale production of titanium seems to be that by W. Kroll (*Trans. Electrochem. Soc.*, **78**, 35 (1940)), which involves the reduction of titanium tetrachloride with fused magnesium at about 800°C. The fabrication and physical properties of ductile titanium are described by R. S. Dean and co-workers (*Trans. Amer. Soc. Mech. Engrs.*, **166**, 382 (1940)). It can be rolled in sheets, swaged into rods, and drawn into fine wire. Pure titanium is normally a very active metal, but small rods or wire from this metal can be heated in air for 20 minutes to 1 hour at 600°C. without excessive oxidation. At higher temperatures it tends to burn. The metal does not react with water at ordinary temperatures. Such acids as acetic, hydrochloric, hydrofluoric, nitric, and sulphuric dissolve it. (See *Titanium: Its Occurrence, Chemistry and Technology*, by Jelks Barksdale (The Ronald Press Co., New York); *Rarer Metals*, by Jack DeMent and H. C. Dale (Chemical Publishing Co., Brooklyn).)

Titanium forms three **oxides**, namely, the dioxide ( $\text{TiO}_2$ ), a white solid, and the sesquioxide ( $\text{Ti}_2\text{O}_3$ ), a red to black solid, both oxides being insoluble and highly refractory; and the trioxide ( $\text{TiO}_3$ ), yellow to red solution, formed by reaction of titanous salt solutions and hydrogen peroxide, and its formation can be used as a test for either chemical. The first two oxides are used in the preparation of enamels to make them resistant to corrosion. The dioxide is used in porcelain glazes, and can be employed in the manufacture of glasses of high heat-resisting and durable character by incorporating it to replace certain proportions of soda, the viscosity increasing proportionally. Titanium oxide is an excellent paint pigment.

A process for producing titanium dioxide from its ores consists of heating them with carbon in a rotary kiln furnace and treating the product with ferric chloride, thus forming ferrous chloride and leaving an insoluble residue of titania, which is subsequently purified by conversion into sulphate, leaching with cold water, and hydrolysing the solutions, causing the precipitation of metatitanic acid ( $\text{H}_2\text{TiO}_3$ ).

The growing importance of titanium dioxide as a pigment has led to a process being worked in Norway for the production of this compound on a considerable scale from *ilmenite* (titaniferous iron ore). It is obtained also to some extent as a by-product in the process for extracting aluminium from bauxite at Katin in India. As compared with white-lead and zinc oxide, "titanium white" (a combination of

26.5 per cent. titanium oxide and 73.5 per cent. barium sulphate) offers considerable advantages, possessing a greater covering power, being non-poisonous, chemically inert, without saponifying action upon linseed oil, and does not blacken upon exposure. A durable paint pigment is a mixture of 80 per cent. titanium white with 20 per cent. zinc oxide. The resinates and linoleates of cobalt and manganese are good siccatives for use with titanium paints (0.2 per cent. manganese or 0.03 per cent. cobalt).

Paints containing titanium pigments are described as elastic, and do not crack or scale after long weathering ; moreover, the titanium pigments have a high covering and oil-absorption power. (See "Titanox.")

"Ready-to-use" paints are stated to be compounded of from 52 to 62 per cent. white titanium pigment, with from 48 to 38 per cent. oil respectively. (See "Titanox.")

**Titanic Acid** ( $\text{H}_2\text{TiO}_3$ ) is a white powder, insoluble in water, but soluble in mineral acids and alkalis, and used as a mordant in dyeing.

**Titanous Chloride** ( $\text{TiCl}_3$ ) can be prepared, among other methods, in the form of violet crystals by reduction of the tetrachloride with hydrogen, and is used commercially in connection with the dyeing of cotton goods when "over-dyeing" has occurred and they require "stripping" before re-dyeing. There is also an oxychloride ( $3\text{TiCl}_4 \cdot \text{TiO}_2$ ).

**Titanium Oxalate** ( $\text{Ti}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ ) is a yellow, crystalline salt, soluble in water, used as a mordant in textile dyeing.

**Titanium Sulphate** ( $\text{Ti}_2(\text{SO}_4)_3$ ) is a white crystalline salt, soluble in hot water, and used as textile mordants.

**Titanium Tetrachloride** ( $\text{TiCl}_4$ ), a colourless liquid of b.p.  $136^\circ \text{C}.$ , made by heating the dioxide and carbon to redness in a current of chlorine, used for making smoke-screens (white) by reaction with the moisture of the air, and in association with potassium bitartrate as a mordant.

**Titanium Potassium Oxalate** ( $\text{TiOC}_2\text{O}_4 \cdot \text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ), commercially known as "T.P.O.," is an important aid to the leather dyer and stainer, as it can be used as a fixing agent previous to dyeing with basic colours and in conjunction with acid colours, the colours so produced ranging from a bright yellowish-brown to a reddish-yellow.

**Titanium sodium sulphate** ( $\text{Ti}_2(\text{SO}_4)_3 \cdot \text{Na}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ ) and **titanous thiocyanate** ( $\text{Ti}(\text{CNS})_3$ ) are used as mordants for cotton, wool, paper, etc.

**"TITANOX"** — A pigment described as titanium dioxide precipitated upon a base of finely divided *blanc fixe*, nearly as white as "French-process" zinc oxide, resistant to sunlight and to hydrogen sulphide. There are various grades, varying from 25 to 35 per cent.  $\text{TiO}_2$ . A compound pigment of zinc oxide 30 per cent. and "Titanox" 70 per cent. has proved good in exposure tests as regards cleanliness from dirt collection.

**TITRATION** — See Reagents, and Volumetric Analyses.

**TOBACCO** — The tobacco plant, of which there are many species, belongs to the genus *Nicotiana* (N.O. Solanaceæ). It is grown in many

countries, including Virginia and other parts of the United States, Rhodesia, Nyasaland, Canada, Turkey, Greece, Bulgaria, Brazil, Mexico, Sumatra, Manila, and North Borneo. The United States is the largest producing country. The *N. tabacum* gives the American tobacco, the *N. rustica* yields the Turkish and other varieties, and the *N. persica* the Shiraz tobacco. From experiments made in Hampshire it would also appear that tobacco can be grown in England to advantage. The quality of tobacco, as also the nicotine content, varies with climate and soil, so that the Turkey-grown product has an entirely different aroma from that grown from the same seed in California, while plants grown in Cuba and transplanted into Florida with Cuban soil around the roots mature with a different quality of leaf. Among other considerations, the ratio of ammonia, phosphoric acid, and potash in the fertilizer is of great importance.

It is alleged that the only practicable way of rendering the nicotine content of tobacco harmless without detracting from the aroma is by treatment with iron salts or certain organic acids which render the nicotine non-volatile (M. Popp).

There is no one special tobacco pest corresponding to the boll-weevil of cotton, but a long list of attacking insects, particularly the leaf-eating caterpillars, including noctuids such as *Prodenia* and *Heliothis*, the hawk-moth caterpillars of the genus *Protoparce*, the surface caterpillar group of the genera *Agrotis* and *Euxoa*, and the leaf-eating genus *Pathorimæa*—the only specialized tobacco pest. The dried fermented leaf is the special food of the world-wide pest, the tobacco beetle (*Lasioderma serricorne*). For the preservation of tobacco against mould spoilage, use is made of acetic acid, but steam sterilization is preferable.

"Offal" tobacco is used for the extraction of nicotine for use in the preparation of sheep-dips, etc., and various substances are used for the purpose of de-naturing the offal, including asafoetida, sulphur, tar acids and oils, lamp-black, bone oil, etc. According to Gabel and Kiprianov, about 96 per cent. of the nicotine contained in tobacco dust can be extracted by kerosene at 80° C. (See Cigarette and Cigar Tobaccos," in *Ind. Eng. Chem.*, **26**, 970 (1934); *Chemistry of Tobacco and Manufactured Tobacco Products*, by A. A. Schmuck (Krasnodar: State Institute for Tobacco Investigations); *The Production of Tobacco*, by W. W. Garner (The Blakiston Co., Philadelphia); and Nicotine.)

**TOBACCO-SEED OIL**, from Kentucky tobacco, is reported to contain 37.68 per cent. fat, consisting of about 52.4 per cent. olein, 22.1 per cent. linolein, and 23.9 per cent. palmitin, and to have a sp. gr. at 15° C. of 0.9404, sap. v. 196, and i.v. 132.8. Dalmatian tobacco-seeds are stated to yield 35.4 per cent. oil, of sp. gr. 0.9250 at 15° C., sap. v., 196.4, and i.v. 131.6.

Tobacco-seed oil resembles cotton-seed oil in many respects, and a quality of edible oil of good flavour may be prepared from it, 100 kilograms of raw oil yielding from 30 to 35 kilograms of refined oil, the seed per acre averaging 1,000 to 1,200 kilograms.

**TÔHAKU OIL**, from the seeds of *Lindera obtusiloba*, found in Korea, is

yellowish-brown in colour, of sp. gr. 0.9329, solidifying at  $-14.4^{\circ}\text{C}.$ ; sap. v. 263.8, and i.v. (Wijs) 70.82. It contains capric and lauric acids, and is used as hair-oil. It is stated to yield an unsaturated fatty acid (linderic acid) with an i.v. of 126.33 and sp. gr. of 0.9246.

**TOLIDINE (3, 3'-Dimethylbenzidine)**  $((\text{C}_6\text{H}_3)_2(\text{CH}_3)_2(\text{NH}_2)_2)$  — A colourless crystalline body of m.p.  $128^{\circ}\text{C}.$ , soluble in alcohol and ether; prepared by reduction from orthonitrotoluene, and used in making the red substantive dye, benzopurpurine 4B.

**TOLU** — See Balsams.

**TOLUENE or METHYL BENZENE (Toluol)**  $(\text{C}_6\text{H}_5\text{CH}_3)$  — An aromatic hydrocarbon of sp. gr. 0.8670, being a benzene derivative of b.p.  $110.6^{\circ}\text{C}.$ ; m.p.  $-95^{\circ}\text{C}.$ , soluble in alcohol, ether, and benzene. It can be obtained as a fractional distillate from coal-tar light oil, by a petroleum cracking process, or by heating toluic acid with lime, and from tolu resin by dry distillation. Oxidized by nitric acid or chromic anhydride, it yields benzoic acid. It finds use as a solvent, in perfumery, as an intermediate, and in the preparation of "T.N.T." explosive and dyestuffs. (See Coal, Explosives, and Hydrocarbons.)

**TOLUENESULPHONAMIDES**  $(\text{CH}_3.\text{C}_6\text{H}_4.\text{SO}_2\text{NH}_2)$  — White crystalline substances; the *ortho* compound is used in the manufacture of saccharin, and the *para* of chloramine T.

**TOLUENESULPHONYLCHLORIDE**  $(\text{CH}_3.\text{C}_6\text{H}_4.\text{SO}_2\text{Cl})$  — The *para* variety is a crystalline body of m.p.  $69^{\circ}\text{C}.$ , soluble in alcohol and ether, used for treating swollen cotton in the presence of indifferent solvents, in order to convert the external fibres into a resistant sulphoester or "immune yarn," which behaves chemically like acetyl silk with certain dyes. It is used in a laboratory method for distinguishing and separating primary from secondary amines.

**TOLUIC ACID** (*meta*, *ortho*, and *para* varieties)  $(\text{CH}_3.\text{C}_6\text{H}_4.\text{COOH})$  — Homologue of benzoic acid. See Acids (Table).

**TOLUIDINE**  $(\text{CH}_3.\text{C}_6\text{H}_4.\text{NH}_2)$  exists in three isomeric forms. The solid *para* compound is a white, lustrous substance (contained in commercial aniline), m.p.  $45^{\circ}\text{C}.$ , from which many red and violet dyes are prepared. The *ortho* and *meta* compounds are liquids which boil at about  $198^{\circ}$  and  $203^{\circ}\text{C}.$  respectively.

**TOLUOL (Toluole)** — Commercial toluene, obtained from the distillation of coal tar; also found in certain natural petroleum, and produced by "cracking" mineral oils; used as a source for making benzyl alcohol, and as a solvent. (See Coal, Petroleum, Solvents, and Toluene.)

**TOLUYL** — The radical group  $\text{C}_6\text{H}_4(\text{CH}_3)\text{CO}-$  of toluic acids (*ortho*, *meta*, and *para*).

**TOLYLENEDIAMINE (Meta)**  $(\text{C}_6\text{H}_3(\text{CH}_3)(\text{NH}_2)_2(1, 2, 4))$  — A colourless, crystalline intermediate soluble in water and alcohol, of m.p.  $99^{\circ}\text{C}.$

**TOLYL** — The monovalent radical group  $-\text{C}_6\text{H}_4(\text{CH}_3)$  of toluene.

**TOMATO-SEED OIL**, expressed from the dried seeds of the tomato (*Solanum lycopersicum*), a native of S. America, particularly Peru, and cultivated in many countries; is yellow; sp. gr. 0.92, sap. v. 191.6, and i.v. 114; miscible with benzol and carbon disulphide, and used in soap-making.

“**TONITE**” — See Explosives.

**TONKA-BEANS (TONQUIN-BEANS)** — The fruit of *Dipterix odorata* and other species of the N.O. Papilionaceæ, indigenous in Guiana and grown in Malaya, containing coumarin and other substances; used in perfumery and for flavouring foodstuffs, etc. The Brazilian bean is known as cumarú kernel, which yields about 30 per cent. of oil. The non-drying oil expressed from the seeds is of sp. gr. 0.878; m.p. 7.2° C.; sap. v. 198.5; i.v. (Wijs) 72.6; ref. ind. 1.4680 at 27° C.; acid v. 1.0; unsaponifiable 0.5 per cent. (See Coumarin.)

**TOPAZ** — A hard, translucent, aluminosilicate mineral containing fluorine in combination, occurring in gneiss or granite, and varying in composition from  $(\text{AlF})_2\text{SiO}_4$  to  $(\text{AlOH})_2\text{SiO}_4$ , of crystal system No. 4, and sp. gr. from 3.35 to 3.65; used for making gems. Varieties occur in Russia, United States, Great Britain, and many other parts of the world, but the best specimens come from Brazil.

**TORBANITES** — Natural products resembling oil shale, the deposits varying in quality, some giving up to 96 gallons and others only 25 to 30 gallons per ton. Extensive deposits exist in Pictou County in Nova Scotia and in parts of Africa, while small deposits occur in Somerset in connection with the coal-beds. The yield is from 60 to 80 gallons of oil per ton. There is a plant at New Glasgow, Nova Scotia, for utilization of the local deposits, in which the rock is heated in an air-tight retort of Mr. J. Ginet's invention, and the resulting gases condensed, each ton of torbanite yielding from 40 to 60 gallons of petroleum. (See Kukkersite, Petroleum, and Shale.)

**TORBERNITE** — A rare mineral represented as  $(\text{CuO} + 2\text{U}_2\text{O}_3)\text{P}_2\text{O}_5 \cdot 8\text{H}_2\text{O}$ , associated with pitchblende, and a source of radium. (See Chalcolite.)

“**TORNESIT**” — A chlorinated rubber base, white, inodorous, non-inflammable, inert to chemicals, and miscible with most plasticizers and common gums. It possesses good dielectric properties, and is highly impermeable to water. Used in paints, emulsions, binders, plastics, and adhesives, and as a rust-preventive.

**TORRICELLIAN VACUUM** — Space above the mercury in a barometer.

**TOTAQUINE** — A mixture of the total alkaloids extracted from cinchona bark, containing not less than 70 per cent. of crystallizable alkaloids of which not less than one-fifth is quinine. It has been used in place of quinine for the treatment of malaria. (See Cinchona.)

**TOURMALINE** — Name of a group of rhombohedral double silicates of aluminium and other bases found in granite, gneiss, or mica-slate, the colours varying with composition. When a crystal (crystal system

## TOURMALINE — TRANSFORMATION TEMPERATURE 1091

No. 3, and sp. gr. about 3.0) of tourmaline is heated to about 150° C. it becomes strongly electrical. If a crystal of tourmaline is not parallel to the axis of the crystal, and light allowed to pass through the slice, the light appears to the eye unchanged, except that it is usually coloured green. If another such slice of crystal is superimposed on the first and one of the slices is rotated while the other remains stationary, then when the axes of the two slices are parallel light passes apparently unchanged, but when the axes are at right angles no light passes. Light has been polarized (see Polarization) in passing through the first slice of crystal, and the second slice extinguishes the extraordinary ray that passes the first slice.

**TOWER FILLINGS** — See Packed Towers.

**TOXALBUMINS** — Products of protein origin distinct from ptomaines, including the poisons of snake bites and others of plant origin, such as abrin (poisonous principle of *Abrus precatorius*—jequirity) and ricin (poisonous ingredient of the castor oil plant).

**TOXAPHENE (Chlorinated Camphor)** — An insecticide.

**TOXIC CHEMICALS** — See Hazardous Chemicals.

**TOXICOLOGY** — See Biochemistry, Poisons, and Vaccines.

**TOXINS** — Substances produced by certain classes of bacteria, responsible for the pathological effects of infection with such organisms. Toxins which are released into a fluid culture medium are known as *exotoxins* whilst those which are retained within the bacterial cell are called *endotoxins*. Soluble exotoxins can be used as immunizing agents since, on introduction into the blood stream, they induce the formation of antitoxins which protect the animals from future infection. Toxins, however, are too poisonous for use in medicine but they can be converted to toxoids, having lowered toxicity but unimpaired immunizing power. Toxin can usually be converted to toxoid by treatment with formaldehyde. In the case of diphtheria prophylactic, various combinations of toxoid are used; these include toxoid-antitoxin floccules (T.A.F.), toxoid-antitoxin mixture (T.A.M.), formol toxoid (F.T.), and alum-precipitated toxoid (A.P.T.). (See Albumins, Bacteria, and Ptomaines.)

“**T.P.O.**” — Titanium Potassium Oxalate. (See Titanium.)

**TRACER** — See Nuclear Chemistry.

**TRAGACANTH** — See Gums and Resins.

“**TRAGASOL**” — A tough jelly made from the carob bean. (See Locust Kernel, and Gums and Resins (Gum Tragon).)

**TRANSFORMATION OR TRANSITION TEMPERATURE** — The temperature at which one crystalline form of an element or compound changes to another crystalline form, or better, that temperature at which both crystalline forms are in equilibrium with each other.

## 1092 TRANSFORMATION TEMPERATURE — TRICHOTHECIN

Sodium sulphate anhydrous ( $\text{Na}_2\text{SO}_4$ ) changes to sodium sulphate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) at  $32.383^\circ\text{C}$ . (Richards, 1898 and 1903); manganese dihydrate ( $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ ) changes to manganese tetrahydrate ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ ) at  $58.089^\circ\text{C}$ . (Richards, 1907); white tin is stable above  $18^\circ\text{C}$ . and grey tin below  $18^\circ\text{C}$ .; monoclinic sulphur is stable above  $96^\circ\text{C}$ . and rhombic sulphur below  $96^\circ\text{C}$ . (See Allotropy, and Matter.)

**TREACLE** — See Molasses.

**TRIACETIN (Glyceryl Triacetate)** ( $\text{C}_3\text{H}_5(\text{OOCCH}_3)_3$ ) — A narcotic poisonous glyceride prepared by heating glycerol with acetic anhydride alone or in presence of finely divided potassium hydrogen sulphate; sp. gr. 1.161, b.p.  $258^\circ\text{C}$ ., miscible with alcohol, ether, chloroform, and benzene. It is used as a plasticizer, also for gelatinizing and lowering the freezing-point of nitroglycerine. (See Acetin.)

**"TRIAZOL"** — See Leptazol.

**TRIBASIC SODIUM PHOSPHATE** — See Sodium (Phosphates).

**TRIBUTYL PHOSPHITE** (Du Pont) — A colourless liquid, of freezing point below  $-30^\circ\text{C}$ ., and sp. gr. 0.934. Used at a concentration of about 0.5 per cent. in oils as a mild antioxidant, and also as a film-strengthening agent.

**TRICHLOROACETIC ACID** ( $\text{CCl}_3\text{COOH}$ ) — A deliquescent, colourless, crystalline compound of m.p.  $58^\circ\text{C}$ . and b.p.  $195^\circ\text{C}$ ., and highly ionized (contrast to acetic acid). It may be prepared by exhaustive chlorination of acetic acid, or by the oxidation of chloral using nitric acid; and by boiling with water it produces carbon dioxide and chloroform. It is used in medicine.

**"TRICLENE"** — See Trichloroethylene.

**TRICHLOROETHYLENE** ( $\text{CHCl} : \text{CCl}_2$ ), a colourless liquid of sp. gr. 1.47 and b.p.  $87^\circ\text{C}$ ., can be made from tetrachlorethane by the action of calcium hydroxide, and yields a very pure monochloroacetic acid by decomposition with sulphuric acid, suitable for use in the production of synthetic indigo. It is non-inflammable, and used as a solvent, especially in the extraction of oil from seeds. Trade-mark is "Triclene" (Du Pont). (See Ethylene Dichloride, and Solvents.)

It is also used in medicine as an analgesic, for which purpose it is inhaled from special inhalers, and also as an anæsthetic in midwifery (the advantage of trichloroethylene in this instance is that it can be administered by the midwife with the aid of a portable apparatus).

**TRICHOTHECIN** — An antibiotic isolated from cultures of *Trichothecium roseum*, being a colourless, crystalline solid of possible empirical formula,  $\text{C}_{15}\text{H}_{18}\text{O}_4$  or  $\text{C}_{15}\text{H}_{20}\text{O}_4$ ; slightly soluble in water giving a neutral solution; soluble in alcohol, chloroform, acetone, and benzene; m.p.  $118^\circ\text{C}$ . It possesses an activity against Fungi Imperfecti, Zygomycetes and Ascomycetes. (See G. F. Freeman and R. I. Morrison, *Nature* (Lond.), **162**, 30 (1948), and *Biochem. J.*, **44**, 1 (1949).)

**TRICRESYL PHOSPHATE** ( $\text{PO}(\text{OC}_7\text{H}_7)_3$ ) — The clear, colourless, liquid, commercial ester, used as a plasticizer for cellulose nitrate, is a mixture of isomers having a sp. gr. 1.177 to 1.180, boiling range  $430^\circ$  to  $440^\circ$  C., flash-point  $215^\circ$  C., and ref. ind. 1.561 to 1.562 at  $20^\circ$  C.; soluble in amyl acetate, acetone, benzene, etc. It is only sparingly soluble in gas-liquor and has been found to present advantages over benzene for the extraction of phenol. A given quantity will extract from 10 to 20 times as much as benzene and owing to the high boiling-point of the solvent, the recovery of the phenol is much simpler, it being merely necessary to distil it off, rendering the tricresyl phosphate ready for use over again. The ortho-compound is a solid of m.p.  $18^\circ$  C. and sp. gr. 1.185 to 1.189; the meta-compound a liquid of sp. gr. 1.178; the para-compound a crystalline solid of m.p.  $76^\circ$  to  $78^\circ$  C. (See *Pyroxylin Enamels and Lacquers*, by S. P. Wilson (Constable and Co., London)).

**TRIDYMITE** — A rare, very hard, mineral form of crystalline silica, of sp. gr. about 2.25, frequently occurring in volcanic rocks. (See Silicon.)

**"TRIELINE"** — See Solvents.

**TRIETHANOLAMINE** ( $\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$ ) — A clear, viscous, hygroscopic liquid, of sp. gr. 1.124, of mildly alkaline character, and used as an emulsifier of oils, etc., in the preparation of cleansing soaps, the manufacture of synthetic resins, and as a gas absorbent.

**TRIETHYLAMINE** ( $(\text{C}_2\text{H}_5)_3\text{N}$ ) — An oily alkaline liquid, of b.p.  $89^\circ$  C. and ionization constant as a base  $4.4 \times 10^{-4}$ . (See Amines.)

**TRIGLYCERIDES** — See Fats.

**TRILENE** — The medicinal name for trichloroethylene.

**TRIMETHYLAMINE** ( $(\text{CH}_3)_3\text{N}$ ) — A gaseous tertiary, aliphatic amine, b.p.  $3.5^\circ$  C., and ionization constant as a base  $5.9 \times 10^{-6}$ . (See Amines.)

**TRIMETHYLENE GLYCOL** ( $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$ ) — See Glycerol.

**TRINITROGLYCERINE** — See Explosives.

**TRINITROTOLUENE** — See Explosives.

**TRIOLEIN** — A principal constituent of olive oil. (See Fats.)

**TRIONAL** — See Methylsulphonal.

**TRIPALMITIN** — See Fats, and Palmitin.

**TRIPHENYLMETHANE** ( $\text{CH}(\text{C}_6\text{H}_5)_3$ ) is a colourless crystalline substance, m.p.  $93^\circ$  C., b.p.  $359^\circ$  C.; readily soluble in hot alcohol, ether, and benzene. Its derivatives include the malachite green, rosaniline, aurine, and the eosin groups of dyes.

**TRIPHENYLMETHYL** — See Radicals (Free).

**TRIPHENYL PHOSPHATE** ( $\text{PO}(\text{OC}_6\text{H}_5)_3$ ) — A colourless, odourless, and somewhat deliquescent, crystalline substance, used as a camphor substitute in making "dope" and impregnating roofing-paper, and as a plasticizer for cellulose acetate, nitrocellulose, and cellulose mixed esters; m.p.  $50^\circ$  C.; b.p.  $220^\circ$  C. at 5 mm.; soluble in alcohol, *n*-butanol, acetone, amyl acetate, *n*-butyl acetate, ethyl acetate, ether, benzene, toluene, and ethylene dichloride.

**"TRIPLEX"** — A glass made to decrease splintering under impact. (See Glass (Laminated).)

**TRIPOLI (Tripolite)** — Impalpable siliceous earth resulting from the natural decomposition of *chert* or siliceous limestone, used as an abrasive and polishing powder. When pure it is white, and most of the grains are less than 0.01 mm. in diameter. (See Diatomite, and Kieselguhr.)

**TRISODIUM PHOSPHATE** — See Sodium (Phosphates).

**TRISTEARIN** — See Stearin, and Fats.

**TRITIUM** — Nucleus of hydrogen isotope, mass 3, charge 1 positive. The high ratio of mass to charge makes it exceedingly effective in penetrating a target nucleus. Produced artificially, tritium is radioactive, decaying to form helium-3 by the emission of a negative beta-particle of low (0.01 Mev) energy.

**"TRITOLITE"** — The trade name of a sodium soap used for separating the parts of emulsions of oil, water, and asphaltic substances, etc.

**TRITURATION** — Grinding to a very fine powder.

**TRIVALENT** — See Valencies.

**TRONA** ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) — Monoclinic crystals, colourless when pure, of sp. gr. 2.112. Incorrectly called sodium sesquicarbonate. Occurs as a natural deposit at Wadi Atrun, Egypt; Lake Magadi, Kenya Colony; Owens Lake, California; and elsewhere. Impurities may include sodium chloride and fluoride, potassium and boron salts, as well as insoluble matter. At Lake Magadi soda ash has been made from trona on a large scale since 1919. The Wadi Atrun, Owens Lake, and other deposits have also been worked commercially.

**TROPANE DERIVATIVES** — Derivatives of the base tropane,  $\text{C}_8\text{H}_{15}\text{N}$ . Among the more important compounds are atropine, hyoscyamine, homatropine, scopolamine and cocaine. (See *Organic Chemistry*, by Paul Karrer (Elsevier Publishing Co., New York).)

**TROPINE** — See Atropine.

**TRYPANOCIDES** — Substances possessing activity against trypanosomes, the causative organisms of sleeping sickness and other human and animal diseases. Trypan Red, a naphthalene dyestuff, was first investigated by Ehrlich for its trypanocidal activity, but it proved disappointing when tested against natural infections in animals. Subsequently, Mesnil introduced Afridol Violet, a complex urea derivative, which was more promising and formed the basic structure of Suramin (Germanin, Bayer 205) which is one of the most effective drugs in this group. Another group of drugs having trypanocidal activity consists of the diamidines, which were developed following the initial discovery that synthalin possessed activity against trypanosomes. These include pentamidine and stilbamidine. Of the organic com-

pounds of arsenic, tryparsamide possesses trypanocidal properties and is used in medicine for this purpose. Antrycide, a salt of 1,1'-dimethyl-4-amino-6-(2'-amino-6'-methylpyrimidyl-4'-amino)-quinaldine, has a curative effect against infections due to *Trypanosoma congolense* and a number of other experimental trypanosomal infections. It possesses prophylactic properties and may prove to be of value in protecting animals against infection in parts of Africa in which cattle-rearing has previously been impossible. For a description of Antrycide, see *Nature* (London), **1**, 89 (1949). (See Pentamidine, Suramin, and Tryparsamide.)

**TRYPARSAMIDE** ( $C_8H_{10}O_4N_2AsNa, \frac{1}{2}H_2O$ ) — A colourless, crystalline organic derivative of arsenic, namely, sodium *N*-phenylglycine-amide-*p*-arsonate, containing 25 per cent. of arsenic; soluble in water, insoluble in alcohol, ether, and chloroform. It is used in medicine as a trypanocide for the treatment of sleeping sickness and for syphilis of the central nervous system.

**TRYPSIN** — An enzyme (digestive ferment) contained in the pancreas, capable of changing albuminous matters into so-called albumoses, in which partially hydrolysed and more soluble state they become converted into peptone. (See Enzymes, Peptones, and Zymogens.)

**T'SAI YU (Ching Yu)** — The name of a vegetable oil obtained by primitive methods from the seeds of certain cabbage plants (*Brassica juncea* and *Brassica campestris*), used for common cooking purposes in China.

**TSUBAKI OIL** — See Tea-Seed Oil.

**T-T-T CURVE OR DIAGRAM** — A graphical representation of a series of isothermal reactions or time-temperature-transformational behaviours of austenite in either plain or alloy steels. Sometimes they are called S-Curves because of their general shapes. For additional information, see "Isothermal Transformation of Austenite," by A. Hultgren (*Trans. Amer. Soc. Metals*, **39**, 915 (1947)), and "Heat Treating Diagrams" by F. R. Morral (*Metal Progress*, **48**, 818 (1945)). (See Iron (Steel).)

**d.-TUBOCURARINE CHLORIDE** ( $(C_{38}H_{44}O_6N_2)Cl_2$ ) — A white crystalline alkaloidal salt, isolated from Tube Curare, moderately soluble in water, m.p. 274° to 275° C. One method of extraction is to dissolve the drug in dilute tartaric acid, precipitate some of the impurities with sodium bicarbonate, which are then removed by extraction with chloroform and ether, and precipitate the quaternary bases remaining in the aqueous liquid with phosphotungstic acid. The precipitated phosphotungstates are decomposed with a hot solution of barium hydroxide, and the quaternary bases then precipitated from the aqueous solution as mercuric chloride complexes which are suspended in water and decomposed with hydrogen sulphide. *d*-Tubocurarine chloride is used in medicine to produce muscular relaxation during anaesthesia for abdominal and other surgical operations.

For a description of the constitution of tubocurarine chloride, see H. King, *J. Chem. Soc.*, 1948, 267. A method of assaying curare preparations, using rats, is described by M. G. Allmark and W. M. Bachinski, *J. Amer. Pharm. Ass., Sci. Ed.*, 38, 43 (1949). See also H. O. J. Collier, S. K. Paris and L. I. Woolf, *Nature* (London), 161, 817 (1948); the curare-like action of polymethylene bis-quaternary ammonium compounds by R. B. Barlow and H. R. Ing, *Nature* (London), 161, 718 (1948); D. M. Paton and E. J. Zaimis, *Nature*, (London), 161, 718 (1948); review of the pharmacology of curare and curarizing substances by W. D. M. Paton, *J. Pharm. et Pharmacol.*, 5, 273 (1949); Curare, and "Myanesin."

**TUNA OIL** — See Fish Oils.

**TUNG OIL (Chinese Wood Oil, Hankow Wood Oil)** to the extent of from 40 to 53 per cent. is obtained by pressure of the sun-dried seeds of *Aleurites fordii* or *A. montana*, indigenous in China. It is also expressed in Madagascar, and known there as *Bakoby oil*. It is composed of glycerides, is generally pale yellow in colour, of drying character, cloudy appearance, unpleasant odour, and liable to solidify when kept. Supplies vary in physical characters, but on average the oil solidifies at  $-3^{\circ}\text{C}$ ., has a sp. gr. 0.936 to 0.943; sap. v. 190 to 195; i.v. 165 (Wijs); m.p.  $47^{\circ}\text{C}$ .; acid value about 7; and ref. ind. 1.5097 to 1.518 at  $20^{\circ}\text{C}$ . It comes to the market in various grades, described as colourless, red, black, yellow, etc. (the colourless or "white" variety being the best); and is used as a waterproofing material for paper, and in making varnishes, driers, and linoleum. It contains a proportion of free fatty acids varying from 2 to 4.6 per cent., some olein, and from 71 to 74 per cent. of the glyceride of alpha-elæostearic acid ( $\text{C}_{17}\text{H}_{29}\text{COOH}$ ), but for varnish-making it should be prepared so that the content of free acid does not exceed 1 per cent.

A communication from Japan gives four Japanese varieties of trees furnishing tung oil, namely, (1) the *Aleurites cordata*, (2) *A. fordii*, (3) *A. montana*, and (4) the Bakoby (*A. moluccana*), the seeds and endosperms of which yield as follows:

	1	2	3	4
Oil content in seeds, per cent.	37.77	44.11	37.43	23.61
Oil content in endosperm, per cent.	59.15	66.29	59.78	70.66
Specific gravity at $15^{\circ}\text{C}$ .	0.934	0.9488	0.9372	0.9267
Saponification value	194.79	196.76	194.31	195.13
Iodine value (Wijs)	151.37	157.17	154.85	146.31
Refractive index ( $25^{\circ}\text{C}$ .)	1.5065	1.521	1.5147	1.4785
Acid value	0.47	1.52	0.59	0.80
Reichert-Meissl value	0.39	1.10	0.35	0.71
Unsaponifiable matter, per cent.	0.41	0.59	0.99	0.97

Summarizing their analyses, Steger and Van Loon give the following data:

	Per cent.
Total fatty acids .. .. .	91.3
Saturated fatty acids: Palmitic 3.7	
Stearic 1.2	
Unsaturated fatty acids: Difference .. .. .	4.9
Volatile acids, aldehydes, etc., partially soluble in water	3.4
Oxidized fatty acids .. .. .	trace
Unsaponified portion .. .. .	0.6
Glycerol as $C_3H_2$ .. .. .	4.7

J. Van Loon gives the following figures as representing the composition of tung oil: Glycerin residue, 4.7 per cent.; unsaponifiable matter, 0.5 per cent.; volatile matter, 3.4 per cent.; saturated acids, 4.9 per cent.; oleic acid, 13.6 per cent.; and elæostearic acid, 72.8 per cent. According to an investigation by Bolton and Williams, the amount of polymerizable matter and of the glyceride of elæostearic acid contained in tung oil are one and the same, varying from 71 to 74 per cent.

Tung oil is frequently adulterated with cotton-seed, soy-bean, rapeseed, tea-seed, perilla, lumbang, and other oils. Experimental planting of tung oil trees is being made in various parts of the British Empire, and with the view of obtaining an independent supply of pure oil, trees are now being cultivated in the southern states of America and Hawaii with promising results. The fresh oil is stated to freeze at  $+3^{\circ}\text{C.}$ , but after long periods it may remain fluid, although viscid, as low as  $-20^{\circ}\text{C.}$  In the absence of air, light changes it to a solid, consisting partly of unchanged oil soluble in acetone and insoluble crystalline beta-elæostearin (m.p.  $61^{\circ}\text{C.}$ ). It absorbs oxygen with avidity, polymerizes slowly when heated below  $150^{\circ}\text{C.}$  and out of contact with air, which change proceeds more rapidly at  $200^{\circ}\text{C.}$ , quickly resulting in a jelly, and finally a solid brittle state. There are certain difficulties in controlling the gelation stages of tung oil, but these are stated to disappear largely when it is mixed with linseed oil. Certain substances—for example, naphthenic acid, linseed oil, common resin, and glycerine—prevent the coagulation of tung oil, glycerine (6 per cent.) having the most effect.

In China and Japan the oil is used for varnishing wood and caulking boats, one Chinese varnish or brilliant oil known as “Kwangyui” being made from the oil by admixture with paraffin, while “Ningpo” lacquer is a mixture of the oil with lacquer used for furniture, etc.

**TUNGSTEN (W) and its Compounds** — Atomic weight, 183.92. See Elements for other data. Tungsten occurs in nature as *wolfram* (*wolframite*,  $(\text{FeMn})\text{WO}_4$ ) and *scheelite*, the former term being often used to cover all minerals in which tungsten trioxide is combined with the oxides of iron and manganese which vary widely in proportion; they are found chiefly in proximity to, or mixed with, tin ores. Wolframite 35\*

is heavy, black, of crystal system No. 5, and great specific gravity (7.1 to 7.9) so that it can be easily concentrated from the associated gangue, but not so easily from tin oxide (cassiterite); as, however, it is feebly magnetic, while the cassiterite is not, this property can be used to effect separation when associated. Deposits are found in France, England, Scotland, Cape Province, South Africa, Arizona, Germany, Portugal, Brazil, Australia, Bolivia, China (Kwangsi and Qwantung Provinces), Japan, Chile, Peru, and Argentine; China being the chief source of supplies. A small sample of ore from the Waichow district was found to contain 55.84 per cent. tungsten, 13.25 per cent. iron, and 11.56 per cent. manganese. Scheelite, or calcium tungstate ( $\text{CaWO}_4$ ), is a heavy yellowish or brown-purple mineral, wax-like in appearance, of crystal system No. 2, and sp. gr. about 6.0; but the supply is small as compared with wolframite. It is chiefly used in the manufacture of ferro-tungsten, on account of the practical difficulties experienced in isolating the oxide for the preparation of pure metallic tungsten. Supplies come from the United States, Bolivia, Portugal, Burma, Malaya, Australia, New Zealand, and Cornwall.

#### TUNGSTEN CONCENTRATES, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

				Tungsten Concentrates as 60% $\text{WO}_3$ , Metric Tons	
Country					
Portugal	..	..	..	2,900	
United Kingdom	..	..	..	200	
Sweden	..	..	..	200	
					3,300
U.S.A.	..	..	..	3,300	
Mexico	..	..	..	100	
					3,400
Bolivia	..	..	..	2,500	
Argentina	..	..	..	1,000	
Peru	..	..	..	100	
					3,600
China..	..	..	..	14,300	
Burma	..	..	..	6,000	
Korea	..	..	..	2,000	
Malaya	..	..	..	1,000	
Indochina	..	..	..	600	
Thailand	..	..	..	200	
					24,100
Southern Rhodesia		..	..	300	
Union of South Africa		..	..	100	
					400
Australia	..	..	..		1,000
Sum of above	..	..	..		35,800
WORLD PRODUCTION, approximately the above.					

The direct reduction of the ores, which yields **ferro-tungsten** suitable for most purposes, is effected by mixing the ore concentrates with coal and roasting in an open furnace, 1 ton of 98.5 per cent. metal being yielded by 2 tons of the purer concentrates.

To prepare the metallic powder, the tungsten oxide ( $\text{WO}_3$ ) has to be isolated from associated matters, and this can only be done by chemical processes involving the application of mineral acids or fusion with alkali, both methods being employed in practice. The acid attack is designed to dissolve out the iron, manganese, and other oxides, leaving the tungsten oxide as an insoluble residue; whereas, by furnacing with soda ash, tungstate of sodium is produced, and from this the yellow tungsten oxide can be precipitated by the addition of dilute acid.

About 95 per cent. of the tungsten production is used in making high-speed tool and other alloy steels. The high-speed tungsten-chromium-vanadium steel contains nearly 20 per cent. tungsten, and permanent magnet steel contains 2 to 4 per cent. tungsten. Nickel-tungsten alloys are used as the bases of acid-resisting materials; a lead-antimony-tungsten alloy is used in making firearms of small calibre; a copper-tungsten wire as a substitute for platinum for sealing into glass; and tungsten plating is superior to chromium plating and more resistant.

The **metal** can be obtained by the alumino-thermic reduction of tungstic oxide, or by its reduction with hydrogen gas in quartz or iron tubes at a temperature of  $1,200^\circ\text{C}$ . (See "Thermit" Process.)

According to J. A. M. van Liempt, the pure metal (99.3 per cent.) in powder form may be obtained in up to 80 per cent. theoretical yield by electrolyzing molten sodium tungstate at  $950^\circ\text{C}$ . with a current density of 15 amperes per square centimetre in a quartz crucible, using tungsten electrodes. It can be obtained of about 96 per cent. purity by reduction of the oxide ( $\text{WO}_3$ ) with charcoal; and also by electrolysis of slightly alkaline fused alkali tungstates. Metallic objects, particularly nickel and copper, or other metals coated with them, may be coated with tungsten by electrolysis in an acid electrolyte, such as one consisting of 38 per cent.  $\text{Na}_2\text{WO}_4$ , 32 per cent.  $\text{Li}_2\text{WO}_4$ , 30 per cent.  $\text{WO}_3$ , at over  $900^\circ\text{C}$ ., the coatings being resistant to most acids but not to alkalis.

Tungsten is a hard, grey, heavy, ductile metal of great tensile strength, highly prized for use in hardening and toughening steel specially made for high-speed metal-cutting tools, and (in a very pure state) for making the filaments of incandescent electric lamps filled with an inert gas such as argon or nitrogen. For this latter application, the powdered metal is fused or sintered together in an atmosphere of hydrogen by the passage of an electric current, the tensile strength of the finished wire of 0.0011 inch diameter being given as 270 tons per square inch.

Tungsten filaments were originally made by the Just and Hanaman process from the metallic powder held together by an organic binding material, and, after sintering, squirted so that the particles were held together by incipient fusion. It was later found that if tungsten

be worked, that is, compressed and hammered, when sufficiently hot (avoiding undue heating), it changes in some molecular manner so that it remains ductile when cold, and can be bent, rolled, or drawn hot or cold of sufficiently fine diameter through reduction dies.

Langmuir found that the blackening which occurs in tungsten filament lamps when first made was due to the deposition of a volatile tungsten oxide, and that this is avoidable by the scrupulous exclusion of water vapour. For this purpose a very high temperature is required in the filament, and this is realized by using it of much larger diameter or coiled in the form of a helix. These lamps are more than four times as efficient as the old carbon filament ones.

Finely divided tungsten powder is a catalyzer, at 350° C., for the transformation of ethyl alcohol into ethylene and water (Sabatier).

There are two **oxides** of tungsten, namely, the trioxide ( $\text{WO}_3$ ), a yellow refractory solid and an article of commerce; and the dioxide ( $\text{WO}_2$ ), a brown solid, slightly soluble in concentrated hydrochloric acid and in concentrated sulphuric acids.

There are several **chlorides**, the di-, tetra-, penta-, and hexachlorides, the last two being volatile liquids (b.p. 276° C. and 347° C., respectively).

**Tungstic Acid** hydrate ( $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ ) is a yellow powder, nearly insoluble in water, which can be obtained in a crystalline condition, and finds use as a mordant and for colouring porcelain. It is obtained by heating, in the first place, a mixture of ore and siliceous quartz in the vapour of carbon tetrachloride; the distillate of iron chloride is collected on dry potassium chloride; the carbon tetrachloride vapour is condensed, and that of the tungstic chloride is passed into dilute nitric acid, forming tungstic acid. It is obtainable in colloidal form by adding hydrochloric acid to a solution of sodium tungstate and subjecting to dialysis.

**Sodium Tungstate** ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ), a colourless crystalline body, made as already described, is soluble in water, and used for fire-proofing fabrics and in the preparation of other tungsten compounds.

**Calcium Tungstate** is used in connection with plates for translating X-rays into rays of greater wave-lengths of increased actinic power.

**Tungsten Carbide** is used in making high-speed cutting tools (see Abrasives).

The name of this element accepted (1949) by the International Union of Chemistry is wolfram in accordance with the symbol in use and the Swedish name for "heavy stone," a principal ore. In 1951, it was permitted to British and American Chemists to retain the name tungsten.

(See *The Metallurgy, Properties, and Applications of Tungsten*, by C. J. Smithells (Chapman and Hall, Ltd., London); *Rarer Metals*, by Jack DeMent and H. C. Dake (Chemical Publishing Co., Brooklyn); *Tungsten: Its History, Geology, Ore-dressing, Metallurgy, Chemistry, Analysis, Applications and Economics* (Reinhold Publishing Corp., New York).)

**TURACINE**—A nitrogenous, organic, red colouring matter found in the feathers of the African birds named *turacos*, containing 8 per cent. of

copper, doubtless derived from the local soil, which is known to contain malachite. Apart from the copper constituent, the colouring matter would appear to have much the same composition as the colouring matter of blood.

**TURBIDIMETERS** — Apparatus for measurement of low turbidities of suspensions. (See Photometry.)

**TURKEY RED** — See Madder.

**TURKEY RED OILS** — Sulphated castor oil made by heating 100 parts castor oil with 20 parts concentrated sulphuric acid at not exceeding 30° C., washing the product first with water and then with a solution of sodium sulphate.

Sodium hydroxide solution or ammonia is then added to the washed ricinoleo-sulphuric acid until it gives a clear solution with water, the resulting products being known commercially as "soda-olein" and "ammonia-olein" respectively. They are used in the dyeing, calico-printing, and leather industries, also for greasing wool to be spun.

Pure sodium ricinoleo-sulphate has been separated from the sodium compound. It is readily soluble in water and has the composition expressed by  $\text{SO}_4\text{Na}, \text{C}_{17}\text{H}_{32}\text{CO}_2\text{Na}, \text{H}_2\text{O}$ .

In conjunction with aluminum hydroxide and colouring matters such as alizarin red (Adrianople red), these red oils form lakes and act as fixing agents.

One variety of "Turkey red oil" is prepared from Gallipoli or olive oil derived from the olives which have been allowed to become rancid and then oxidized by exposure to moisture and air.

Advantage is taken of the solvent and emulsifying properties of neutralized castor oil sulphation products in the preparation of a number of water-soluble defatting materials, such as "Tetrapol," "Tetraisol," "Lanapol," and "Verapol," used in the textile industries, these various preparations containing other substances in addition, such as hydrocarbons, chlorhydrocarbons, etc.

**TURMERIC (Curcumin)** — A yellow or saffron colouring matter prepared from the roots of an East Indian plant (*Curcuma longa*, N.O. Zingiberaceæ), cultivated also in China, India, the East Indian Islands, and the Fijis; used for dyeing, also in pharmacy and medicine, as a constituent of curry powder and pickles, and for colouring butter, etc. (See Curcumenes.)

Absorbent paper coloured with a solution of the yellow colouring matter of turmeric is turned brown by alkaline solutions, and is sometimes used in place of litmus paper. (See Volumetric Analyses.)

**TURNBULL'S BLUE** is generally represented as ferrous ferricyanide ( $\text{Fe}_3(\text{Fe}(\text{CN})_6)_2$ ), and is prepared by precipitating a solution of a ferrous salt with potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ). When prepared under certain conditions it is practically identical with Prussian blue. (See Prussian Blue.)

**TURPENTINE** — Oil of turpentine is a colourless, limpid liquid consisting of a mixture of hydrocarbon terpenes obtained by distillation

from the oleo-resin produced in various species of *Pinus* when the sapwood is injured. The crude exudation is collected by making cuts or slits in the bark of the trees, through which the crude turpentine exudes and is collected in metal cups fixed below the cuts. Oil of turpentine is distilled from the oleo-resin and the residue of colophony remains in the retort.

According to the United States Federal Specification for Turpentine for Paint, oil of turpentine commences to distil at 150° to 160° C. at 760 mm. pressure, and not less than 90 per cent. distils below 170° C.; sp. gr. 0.860 to 0.875 at 15.5° C.; ref. ind. 1.465 to 1.478 at 20° C.; after polymerization with 38N H<sub>2</sub>SO<sub>4</sub>, the residue is straw-coloured, viscous, and not more than 2 per cent. by volume, and the refractive index of the residue is not less than 1.500.

American turpentine is obtained chiefly from *Pinus palustris* (Longleaf) and *P. caribaea* (Slash); French turpentine from *P. maritima* and *P. pinaster*; Russian turpentine from *P. sylvestris* and *P. ledebourii*; German turpentine from the Scotch fir, *P. sylvestris* and *Abies pectinata*; Strasburg turpentine from *Abies pectinata*; Venice turpentine from the larch, *Larix Europaea*; Indian turpentine from *P. longifolia* Roxb.; Burma turpentine from *P. Khassya* (corresponding to the American product); and Chian or Chio turpentine from *Pistacia terebinthus* and *Pinus vera*. Indian turpentine from *Pinus longifolia* contains a mixture of terpenes, including the diterpene, carene, C<sub>20</sub>H<sub>32</sub>, and resembles Russian turpentine in susceptibility to oxidation by air. Turpentine is also recovered from digester relief gases during the cooking of pines and it has been stated that this constitutes the source of 23 per cent. of the total production of turpentine in the U.S.A. (see Lawrence, *Paper Trade J.*, 123, No. 15, 95 (1946). The so-called sulphite (spruce) turpentine contains considerable *p*-cymene; and mixtures of this with organic solvents such as acetone, isopropyl alcohol, and other alcohols constitute good paint and varnish removers.

Crude turpentine, as exuded from the trees, finds little use as such, but oil of turpentine is used extensively as a solvent, volatile vehicle, or otherwise in connection with many manufactured articles including synthetic camphor, paints, polishes, leather dressings, varnishes, and it is also used in pharmacy as a constituent of liniments. (See Camphor, Essential Oils, Gums and Resins, Pine Oil, and Terpenes.)

**TURPETH** — See Mercury.

**TURQUOISE** — A gem consisting of hydrated aluminium phosphate (Al<sub>2</sub>O<sub>3</sub>.P<sub>2</sub>O<sub>5</sub>.5H<sub>2</sub>O), of sp. gr. 2.6 to 2.8, coloured by copper and iron oxides, found in certain provinces of Iran, Mexico, etc.

**TUSCAN RED** contains from 40 to 60 per cent. ferric oxide (Fe<sub>2</sub>O<sub>3</sub>), brightened with some organic red dyestuff.

**TWADDELL SCALE** — See Hydrometers.

**TWITCHELL** — See Fats, and Soaps.

**"2,4-D"** — See Herbicides.

**TYNDALL BEAM** — If a strong beam of light is passed through a medium which contains particles no larger than molecules, the medium is said to be optically clear because the path of the light cannot be easily detected by the unaided eye. On the other hand, if particles larger than molecules yet too small to be seen by the best microscopes are present, they will scatter the light and the path of the beam is rendered visible. This is the Tyndall beam.

**TYPE-CLEANING AGENTS** include preparations known as "Cornedol," "Cykloran," "Duferol," "Hexalin," "Nutralan," and "Pinol."

**TYPE METAL** — Alloys of lead, antimony, and tin, with occasionally copper and bismuth. (See Alloys.)

**TYRIAN PURPLE** — A dye obtained in minute quantities from the purple snail, *Murex Brandaris*, native to the shores of Phœnicia, and highly prized by the ancients as a symbol of high rank, the material being so scarce that it was reserved for the dyeing of royal robes; hence the tradition associating the colour with royalty. Tyrian Purple is 6,6'-dibromoindigo, and can be made synthetically, although it is not commercially important.

**TYROCIDIN** — An antibiotic substance related to gramicidin, said to be toxic to several species of bacteria and some fungi. (See Gramicidin.)

**TYROSINE** ( $\text{HO.C}_6\text{H}_4.\text{CH}_2.\text{CH}(\text{NH}_2)\text{COOH}$  (1, 4)) — A crystalline amino-acid obtainable from many proteins by hydrolysis. It is sparingly soluble in cold water, alcohol, or ether, but readily soluble in hot water, dilute acid, or dilute alkalis, and forms esters and salts. M.p.  $295^\circ\text{C}$ . with decomposition. First isolated by von Liebig in 1846. It is the tyrosine residues in proteins which are responsible for the red precipitate obtained with Millon's reagent. Tyrosine is found in the liver in certain diseases, and occurs normally in cheese, the spleen, and the pancreas.

**TYROTHRIN** — An antibiotic substance, being a mixture of gramicidin and tyrocidin, produced by the spore-bearing soil organism, *B. brevis*. It possesses bactericidal activity against Gram-positive organisms but is too toxic for systemic administration. It is used in medicine for local application. (See Gramicidin.)

**UCUÚBA OIL** — Extracted as a yellow fat from the nuts of the ucuúba tree which grows wild in the Amazon area. The kernels of the nuts yield 70 per cent. of edible oil.

**ULEXITE** — See Boron.

**ULLMANITE** — A mineral compound of sulphur, antimony, and nickel, sometimes represented as  $\text{SbNiS}$ , occurring in crystal system No. 1, and of sp. gr. 6.0 to 6.5.

**ULTRA-CENTRIFUGE** — See Centrifuges, Colloidal State, and Particles.**ULTRA-FILTRATION** — See Filters.

**ULTRAMARINE** — A valuable blue pigment of complicated composition containing aluminium in the form of silicate found in Persia and Turkestan and known as *lapis lazuli*. The ultramarine of commerce is made artificially by exposing to a red heat in tightly closed crucibles or muffle furnaces, but below fusing-point ( $750^{\circ}$  to  $800^{\circ}$  C.), a mixture of kaolin or powdered quartz of high purity, sodium carbonate or caustic soda, sulphur, and charcoal (or pitch, tar, or resin), supplemented by some subsequent treatment. Its exact constitution is not known, but it may be regarded as a double silicate of aluminium and sodium in association with sodium sulphide. There are other modified processes of manufacture, and it can be made of various tints, including green, red, and violet. Iron is the most undesirable impurity, of which not more than 0.5 per cent. must be present on account of its darkening effect, and it is very easily decomposed by the slightest trace of acid. Its essential formula has been given as  $\text{Na}_4(\text{NaS}_3\text{Al})\text{Al}_2(\text{SiO}_4)_3$ . Another description gives the "poor in silica and rich in sulphur" blue type as represented by the formula  $\text{Na}_8\text{Al}_6\text{Si}_6\text{S}_4\text{O}_{24}$ , and the "rich in silica and poor in sulphur" type as  $\text{Na}_8\text{Al}_4\text{Si}_6\text{S}_4\text{O}_{20}$ . One mixture used for producing a bright blue product consists of 540 kilograms kaolin, 8 kilograms caustic soda, 538 kilograms soda ash, 268 kilograms sulphur, and 46 kilograms charcoal. Another satisfactory mixture is given as follows:

	Per Cent.					
Kaolin	..	..	..	..	..	30.5
Silica	..	..	..	..	..	6.5
Caustic soda	..	..	..	..	..	0.5
Sodium carbonate	..	..	..	..	..	27.0
Sulphur	..	..	..	..	..	31.5
Carbon	..	..	..	..	..	4.0

The product after cooling is finely ground under water and subsequently dried and sifted. It is used in making laundry blues, mottled soap, paints, colours, and in paper manufacture.

**ULTRA-MICROSCOPE** — See Colloidal State.

**ULTRA-VIOLET RAYS** — Light (health) rays forming the shorter ones (wave length 0.1 to 0.4 microns) of the spectrum lying beyond the violet rays, to which the human eye is not sensitive. They have some bactericidal power, are capable of effecting or intensifying many chemical changes, including bleaching effects on textiles, etc., and causing fluorescence of quinine solutions, honey, etc. They have been successfully applied (by taking advantage of their fluorescent effects) for discriminating between Japanese pearls and other kinds, and vegetable and mineral oils; for determining the purity of many chemicals; for distinguishing between cotton, wool, and silk, various kinds of card and paper, and old masters and faked pictures, as each pigment has its own fluorescence.

A method used for determining the amount of ultra-violet radiation in the atmosphere employs a quartz tube containing a standard solution of acetone and methylene blue exposed at the top of a mast, the amount of bleaching which ensues in the solution by comparison with standardized tubes giving a biological indication. Each degree of the standardized scale is equivalent in value, and represents twice as much radiation as suffices to produce a slight erythema or flushing of the average sort of skin. A measurement of, say, 5 degrees means that the power of the rays from skyshine and direct sun together fades the standard acetone solution exposed in the standard quartz tube 5 points on the scale. Thus in a central part of London on a misty day in December the amount may be nil (owing to loss attributed to smoke pollution), while it may be 23 in open country in July and on an August day in Switzerland as high as 41 degrees.

The light obtained from quartz mercury-vapour, carbon arc, and tungsten arc lamps, respectively, is rich in ultra-violet radiations, and has found application in the treatment of rickets, as a test for colour fastness, for sterilizing water and air, and for distinguishing synthetic from other tannins.

*References* : *Physiological Effects of Radiant Energy*, by Henry Laurens (Reinhold Publishing Corp., New York), *The Spectroscopy of the Extreme Ultra-Violet*, by T. Lyman (Longmans, Green and Co., London) ; *The Chemical Action of Ultraviolet Rays*, by Carleton Ellis and A. A. Wells (Reinhold Publishing Corp., New York) ; also Mercury Lamp, Fluorescence, Photocatalysis, Radioactivity, Vitamins, Wave Lengths, and X-Rays.)

**UMBELLULARIA OIL**, from the nut of the Californian laurel (*Umbellularia Californica* Nutt). (See Laurel Oil.)

**UMBERS (Sienna)** — Pigments used in paint-making, staining, and the paper trade, consisting of natural oxide of iron allied to ochre ; one variety is in the nature of a brown silicated hematite of the composition  $2\text{Fe}_2\text{O}_3, \text{SiO}_2, \text{H}_2\text{O}$ . The deposits vary in colour (from yellow to brown) and in composition, the colouring being attributed to proportions of manganese compounds and alumina. Varieties occur in Italy, England, and other places, and are prepared for the market by grinding, washing, and then drying at  $100^\circ\text{C}$ . Burnt umber is the calcined product, and is darker in colour. (See Ochre, and Vandyke Brown.)

**UNIT OPERATIONS** — See Chemical Engineering.

**UNIT PROCESSES** — These are classified by R. N. Shreve into the following groups by types of reaction : Addition, Oxidation, Reduction, Substitution, Pyrolysis, Polymerization, Condensation. Conditions that should be studied in conducting the reactions are : Temperature, Speed of Reaction, Concentration and Solvents, Phases of Reactants and Products and Size of Solid Particles, Heat Evolution or Absorption, Power Consumed. See *Unit Processes in Organic Chemistry*, by P. H. Groggins (McGraw-Hill Book Co., New York) ; Symposium on Unit Processes in *Ind. Eng. Chem.*, 29, 1329 et seq. (1937) ; Annual

Reviews in September issues of *Ind. Eng. Chem.* since 1948; *The Chemical Process Industries*, by R. Norris Shreve (McGraw-Hill Book Co., New York).

**UNITS** — See Weights and Measures.

**UNIVALENT** — See Valencies.

**UNSATURATED COMPOUNDS** — See Valencies.

**UPAS (Malay Poison)** — Arrow poison used in the East Indies, obtained from the milky juice of the *Upas antjar*, *Upas radja*, and some kinds of *Strychnos*, the best known being said to be prepared from the gum which exudes from incisions in the stem of the anchor tree (*Antiaris toxicaria*).

**URALITE (Amphibole)** — Hornblende from Ural districts. (See Amphibole, Asbestos, and Hornblende.)

**URANINE** ( $\text{Na}_2\text{C}_{20}\text{H}_{10}\text{O}_8$ ) — Sodium fluorescein, a yellow, crystalline dye, obtained by treating fluorescein with sodium carbonate; used also for following the course of subterranean waters, etc.

**URANINITE** — See Pitchblende, and Uranium.

**URANITE** — Uranium minerals, one of which is a phosphate of uranium and copper, and the other a phosphate of uranium and calcium.

**URANIUM (U) and its Compounds** — Atomic weight 238.07. See Elements for other data. Uranium is contained to the extent of from 40 to 90 per cent. as oxide in association with other compounds in the mineral *pitchblende* (*uraninite*), which is found in some Cornish mines, Austria, Colorado, and elsewhere. It also occurs in *bröggerite*, *cleveite*, and *uranite*, and a number of other minerals, including *carnotite*, *fergusonite*, *samaraskite*, etc. *Brannerite* is the name of a uranium mineral found in the pegmatites obtained from gold placer mines in Idaho. It is described as a complex titanate of uranium, associated with smaller quantities of rare earths, including as much as 50 per cent. of uranium oxides. *Sodinite* is the name given to a radioactive silicated uranium mineral found in association with *curite* in the Belgian Congo, and contains about 85.33 per cent.  $\text{UO}_3$ .

The best deposits of uranium ores, apart from the Cornish pitchblende, are those severally found at Joachimsthal in Bohemia, Johanngeorgstadt in Saxony, in Colorado and Utah, in the Belgian Congo, and in the Great Bear Lake region of northern Canada. Deposits of uranium ore are believed to be present in Russian Turkestan on the north slope of Mount Altai, in the area between Och and Samarkand, and near Tabochar in the Karamazan mountains (I.U. Bachilov, 1935).

Uranium was discovered by Klaproth in 1789 and was first isolated as the metal by Peligot in 1842. It was in uranium that Becquerel discovered radioactivity in 1896. Natural uranium is a mixture of three isotopes,  $\text{U}^{234}$  (0.006 per cent.),  $\text{U}^{235}$  (0.71 per cent.), and  $\text{U}^{238}$

(99.28 per cent.).  $U^{238}$  is the parent of the so-called " $4n+2$ " radioactive series and among its decay products are the well-known radium, radon, and polonium.  $U^{234}$  is also a member of this series. Similarly, the isotope  $U^{235}$  is the parent of the actinium series or " $4n+3$ " radioactive series. (See Nuclear Chemistry.)

Uranium metal may be prepared in several ways. One of these is the reduction of any of the anhydrous halides with alkali metals or alkaline earths. It may also be prepared by the electrolysis of uranium salts in fused electrolytes such as sodium fluoride or calcium chloride. Uranium metal melts at  $1,133^{\circ}\text{C}$ . and has a density of 18.49 (U.S. Bureau of Standards). It is a white metal which can be polished, giving a steel-like lustre. It is moderately malleable and ductile. Uranium forms alloys with many metals, such as copper, zinc, magnesium, aluminium, titanium, vanadium, molybdenum, tungsten, and iron. These alloys are usually prepared by aluminothermic reduction of the oxides.

Uranium is the primary material in atomic energy; previous to its use here its usefulness was rather minor. The metal had been utilized in making special steels, and certain of its compounds have been used as stains in the leather and wood industries and for glazes in ceramics. It is now perhaps the most sought after element in the world because of its extreme importance for atomic energy. The important isotope here is the relatively rare  $U^{235}$  which can be made to undergo a nuclear chain reaction resulting in the production of much energy and in the production of the new synthetic element plutonium. The plutonium is formed from the more abundant  $U^{238}$  when it captures neutrons produced in the fission of  $U^{235}$ . Plutonium in turn may be separated from uranium and the products of the nuclear chain reaction and used as the active ingredient in atomic bombs or as a source of atomic power.

Uranium metal stands between aluminium and manganese in the electromotive series and is sufficiently active to decompose water. In the form of powder the metal is extremely pyrophoric when exposed to air. Uranium has four well-established oxidation states. These may be written as  $U^{+3}$ ,  $U^{+4}$ ,  $UO_2^{+}$ , and  $UO_2^{++}$ , representing uranium valences of +3, +4, +5, and +6, respectively. The pentavalent state is the least stable, as it tends to oxidize and reduce itself to the hexavalent and quadrivalent states. The trivalent state is also unstable, as it is easily oxidized. As a result, the chemistry of uranium compounds is largely that of the quadrivalent and hexavalent states.

Among the derivatives of *hexavalent* uranium is the **hexafluoride** ( $UF_6$ ) a yellow solid at room temperature but volatilizing when heated (b.p.  $56^{\circ}\text{C}$ . at 1 atm. pressure). It can be prepared by the reaction of fluorine with the metal or with one of the oxides of uranium. **Uranium trioxide** ( $UO_3$ ) is a yellow solid formed by decomposing the **nitrate** ( $UO_2(NO_3)_2$ ) in an atmosphere of oxygen. This oxide dissolves in acids to form the various uranyl salts. The most insoluble uranyl compounds in slightly acid solution are the double and triple acetates with a variety of metals. The best known of these is **sodium uranyl acetate** ( $NaUO_2(C_2H_3O_2)_3$ ). **Uranium peroxide** may also be prepared

in slightly acid solution by the addition of hydrogen peroxide to a solution of a uranyl salt. In alkaline solution uranyl uranium forms the insoluble **uranates** and **diuranates**.

When uranium metal is dissolved in non-oxidizing acids it forms compounds of the *quadrivalent* state. Uranium metal also combines directly with chlorine to form **uranium tetrachloride** ( $\text{UCl}_4$ ). **Uranium tetrafluoride** ( $\text{UF}_4$ ) is precipitated from acid solution upon the addition of a soluble fluoride. Its melting point is  $1,000^\circ\text{C}$ . The oxide of the quadrivalent state is brown **uranium dioxide** ( $\text{UO}_2$ ) which is stable at very high temperatures but is converted to the "black oxide" ( $\text{U}_3\text{O}_8$ ) at lower moderate temperatures in air. For the radioactive character of uranium, see Nuclear Chemistry.

**URANYL** — The divalent radical  $\text{UO}_2$  of uranyl nitrate and uranic acid ( $\text{UO}_2(\text{OH})_2$ ).

**UREA (Carbamide)** ( $\text{CO}(\text{NH}_2)_2$ ) — A white, crystalline substance known as a constituent of urine, resulting from oxidation of certain nitrogenous bodies in the animal organism, of which an adult man excretes about 30 grams daily. It is soluble in water and alcohol, melts at  $133^\circ\text{C}$ ., sublimates when heated *in vacuo*, and forms compounds with acids and with bases. Ammonium cyanate is easily transformed into urea (with which it is isomeric) by heating, and urea can also be made by the action of ammonia on ethyl carbonate or by the action of mercuric oxide on oxamide.

The value of urea as a fertilizer, containing as it does 46 per cent. nitrogen, has long been recognized. Its use in making synthetic resins, especially with formaldehyde, is important, and it is useful for removing the lustre of cellulose acetate silk. The process for its manufacture from synthetic ammonia and carbon dioxide depends upon the conversion of solid ammonium carbamate by heat, in an autoclave at about  $150^\circ\text{C}$ ., thus:  $\text{NH}_2\text{CO.ONH}_4 = \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O}$ . The carbamate is prepared from its constituents in a gaseous state, and about 40 per cent. is thus transformed and left in a pure state in the still, any carbamate and its gaseous dissociation products which pass over being subsequently recovered. By the use of thoria as a catalyst the yield of carbamate from ammonia and carbon dioxide is much increased, some 50 per cent. of the latter being converted, provided that the ammonia is always present in excess.

Another process reported to give a practically quantitative yield of urea consists of the treatment of cyanamide in strong aqueous solution with an acid catalyst (sulphuric, phosphoric, or nitric acid) at below  $75^\circ\text{C}$ . and under some pressure (using less than 10 per cent. of the amount of acid required to form a salt with the urea), after which the mixture is neutralized with calcium carbonate, filtered, and evaporated. A continuous process for its manufacture from liquid ammonia and liquid carbon dioxide as developed by Krase, Gaddy, and Clark is described in *Ind. Eng. Chem.*, **22**, 289 (1930), and its industrial development and the properties of crystal urea by J. F. T. Berliner in *Ind. Eng.*

*Chem.*, 28, 517 (1936). A patented use for urea is its employment for "carrotting" hair as used for making felt. In addition to its uses as fertilizer and in synthetic resins, urea finds application for adhesives, in animal feeds, in fire-resistant paints, and as an intermediate for certain dyes and pharmaceutical preparations. One ton of nitrogen is contained in every 2.14 tons of urea, as compared with the same content in 4.71 tons of ammonium sulphate and 6.07 tons of sodium nitrate; and it has been found superior to ammonium salts and sodium nitrate as a fertilizer for rubber trees, at the same time acting as a protective against defoliation or so-called "secondary leaf-fall." (See Cyanic Acid, Fertilizers, and Guanidine.)

**UREASE** — See Enzymes.

**UREIDES** — Bodies analogous to the amides, being derivatives of urea with acid radicals such as acetylurea  $\left( \text{OC} \begin{array}{l} \text{NH}_2 \\ \text{NHOCCH}_3 \end{array} \right)$  and oxalylurea (parabanic acid)  $\left( \text{OC} \begin{array}{l} \text{NH-CO} \\ \text{NH-CO} \end{array} \right)$ .

Among the most important ureides are the cyclic ureides used in medicine, such as the hypnotics Barbitone and Phenobarbitone, and the basal anæsthetics, such as Evipan. The open-chain ureides such as Carbromal are no longer used to any extent. The purine derivatives, such as uric acid, caffeine, and theobromine, are often referred to as ureides.

**UREOMETER** — An apparatus for quantitatively determining the amount of urea contained in urine, by measuring the nitrogen gas evolved in its decomposition by sodium hypobromite in sodium hydroxide solution.

**URIC ACID**  $\left( \text{NH.CO.NH.CO.C.NH.CO.NH} \right)$  — A dicyclic ureide occur-

ring in the urine and in the excrement of snakes or birds. It is a white, sparingly soluble, weakly acidic substance, and chemically is 2,6,8-trioxypurine. Purine is the parent of the group known as the dicyclic ureides, and besides uric acid, the group contains caffeine, theobromine, theophylline, adenine, guanine, etc. None of these substances are now regarded as alkaloids, but are best referred to as "purine bases." (See Purine.)

**URINE** — An excretory liquid containing part of the soluble broken-up or waste products of the living organism. It has an average sp. gr. of 1.02, and amounts to from 1,400 to 1,600 cubic centimetres per twenty-four hours, containing dissolved solid matters to the extent of from 50 to 60 grams, small amounts of undetermined and varying constituents, various colouring matters, and mineral salts, including sodium chloride, phosphates, sulphates.

Kryptophanic Acid ( $\text{C}_{10}\text{H}_{18}\text{O}_{10}\text{N}_2$ ) is the normal free acid of human urine, and it has been stated that hippuric acid, which is a normal

constituent of the urine of herbivorous animals, is sometimes, if not always, present in small quantity in the human liquid excretion. (See Thudichum's *Annals of Chemical Medicine*, vol. i., chapter xii. (Longmans, Green and Co., London); Albuminometer, and Ureometer.)

“**URIODONE**” — See Diodone.

“**UROPAC**” — See Iodoxyl.

“**UROSELECTAN B**” — See Iodoxyl.

“**URUMBRIN B**” — See Iodoxyl.

**VACUUM** — See Pressure, Low.

**VACUUM SALT** — See Sodium Chloride.

**VALENCIES** — The atoms of elements (as chemically understood) possess powers of combination, or so-called *valency*, indicative of the number of other atoms with which an atom of an element can directly combine. Hydrogen is a so-called *univalent* or *monovalent* element, that is, it has only one capability of chemical attachment to another element. Thus, it may be made to combine with chlorine (another univalent element) atom for atom, thus:  $\text{H}-\text{Cl}$ .

Other elements are known, where molecular weight determinations show that two atoms of hydrogen are combined with one atom of the other element, thus:  $\text{H}_2\text{S}$  (hydrogen sulphide) and  $\text{H}_2\text{O}$  (water).

These may be represented structurally in this way:  $\begin{array}{c} \text{H} \\ \diagup \\ \text{H} \end{array} \text{S}$  or  $\text{H}-\text{S}-\text{H}$ ,

and  $\begin{array}{c} \text{H} \\ \diagup \\ \text{H} \end{array} \text{O}$  or  $\text{H}-\text{O}-\text{H}$ . The valency of sulphur and of oxygen is said to be two.

Further, still other elements demand, by the same line of reasoning, acceptance of valency figures greater than two. If one subscribes to the electronic interpretation of valency a series such as the following can be made, on the simple assumptions that the valency of hydrogen is plus one, that of oxygen minus two, and so on from these elements, with the known fact of the electrical neutrality of the molecule.

Compound :	HCl	H <sub>2</sub> S	H <sub>2</sub> N	H <sub>4</sub> C				
Electronic								
Valency :	Cl <sup>-1</sup>	S <sup>-2</sup>	N <sup>-3</sup>	C <sup>-4</sup>				
	H <sub>2</sub> O							
Compound :	Na <sub>2</sub> O	CaO	Al <sub>2</sub> O <sub>3</sub>	CO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Mn <sub>2</sub> O <sub>7</sub>	Os <sub>2</sub> O <sub>8</sub>
Electronic								
Valency :	Na <sup>+1</sup>	Ca <sup>+2</sup>	Al <sup>+3</sup>	C <sup>+4</sup>	P <sup>+5</sup>	S <sup>+6</sup>	Mn <sup>+7</sup>	Os <sup>+8</sup>

Whether or not the molecule is symmetrical is possible of testing by measurement of the dipole moment (see same) of vaporizable substances.

Each element has its own characteristic valencies, the total gamut run being apparently from  $-4$  to  $+8$ . Some elements show in different

compounds different valencies, witness chlorine, sulphur, nitrogen, and carbon :

$\text{Cl}^{-1}$ KCl Potassium : Chloride		$\text{Cl}^{+1}$ KOCi Hypochlorite		$\text{Cl}^{+3}$ KOCiO Chlorite	$\text{Cl}^{+5}$ KOCiO <sub>3</sub> Chlorate	$\text{Cl}^{+7}$ KOCiO <sub>4</sub> Perchlorate
$\text{S}^{-2}$ H <sub>2</sub> S Acid, Hydrosulphuric		$\text{S}^{+4}$ H <sub>2</sub> SO <sub>3</sub> Sulphurous		$\text{S}^{+6}$ H <sub>2</sub> SO <sub>4</sub> Sulphuric		
$\text{N}^{-3}$ NH <sub>3</sub> Ammonia	$\text{N}^{-1}$ H <sub>2</sub> NOH Hydroxylamine	$\text{N}^{+2}$ NO Nitric Oxide		$\text{N}^{+3}$ HONO Nitrous Acid	$\text{N}^{+5}$ HONO <sub>2</sub> Nitric Acid	
$\text{C}^{-4}$ CH <sub>4</sub> Methane		$\text{C}^{-3}$ H <sub>3</sub> COH Methyl Alcohol	$\text{C}^0$ H <sub>2</sub> CO Form- aldehyde	$\text{C}^{+2}$ CO Carbon Monoxide HC<O OH Formic Acid	$\text{C}^{+4}$ CO <sub>2</sub> Carbon Dioxide O=C<OH OH Carbonic Acid	

Transformations from one electronic form to another of the same element are accomplished, sometimes with ease and sometimes with difficulty, for example :

With Sodium Sulphite Solution, in each case :	$\text{Mn}^{+2}$ MnCl <sub>2</sub> Manganous Chloride Soluble Pink	$\text{Mn}^{+4}$ MnO <sub>2</sub> Manganese Dioxide Insoluble Brown	$\text{Mn}^{+6}$ K <sub>2</sub> MnO <sub>4</sub> Potassium Manganate Soluble Green	$\text{Mn}^{+7}$ KMnO <sub>4</sub> Potassium Permanganate Soluble Purple
	←———— In acid solution —————→			
	←———— In alkaline solution —————→			
	←———— In neutral solution —————→			
	{			

Such changes of valency are brought about by means of so-called oxidation-reduction reactions.

In contrast to polar valent compounds that dissociate electrolytically in water, such as HCl, there are the covalent compounds, such as methane, where the electrons are shared between atoms. Such covalent compounds are generally soft when crystalline, and of low melting-points.

The doctrine that the space " form " of the carbon atom is that of a regular tetrahedron was originated by Van't Hoff. (See Stereochemistry.)

**Saturated Compounds** are those in which there are no unsatisfied affinities, for example, the normal hydrocarbons (paraffins) of which methane (CH<sub>4</sub>) is typical, the tetravalency of carbon being fully satisfied by combination with 4 atoms of hydrogen. Again, phosphorus pentoxide (P<sub>2</sub>O<sub>5</sub>) is a saturated body, the 2 atoms of phosphorus

(which is pentavalent) being satisfied by combination with 5 atoms of divalent oxygen.

**Unsaturated Compounds** possess unsatisfied affinities, such as phosphine ( $\text{PH}_3$ ), in which three only out of the five affinities are saturated by combination with hydrogen, leaving two unsatisfied. Unsaturated compounds can take up hydrogen, halogens, etc., to produce saturation; thus CO can, by combination with  $\text{Cl}_2$ , become  $\text{COCl}_2$ ; again, ethylene ( $\text{C}_2\text{H}_4$ ) may be regarded as only a half-saturated compound, becoming saturated when converted into ethane ( $\text{C}_2\text{H}_6$ ) or into ethylenedichloride (1,2-dichloroethane) ( $\text{C}_2\text{H}_4\text{Cl}_2$ ).

See *The Parachor and Valency*, by S. Sugden (Routledge and Sons, London); *The Electronic Theory of Valency*, by N. V. Sidgwick (Oxford University Press); *Valency, Classical and Modern*, by W. G. Palmer (Macmillan Co., New York and London); *Modern Chemistry*, by A. J. Berry (Cambridge Univ. Press); *The Theory of Resonance*, by G. W. Wheland (John Wiley and Sons, New York); *The Nature of the Chemical Bond and the Structure of Molecules and Crystals*, by Linus Pauling (Cornell Univ. Press, Ithaca); and Hydrocarbons.

**VALERIAN** — The dried rhizome and roots of *Valeriana officinalis* (Fam. Valerianaceæ), collected in the autumn. The plant is widely distributed throughout Europe and Northern Asia and is cultivated in England, Holland, Germany, and the United States. It contains starch, a resinous substance, and about 1 per cent. of volatile oil. The oil has been used in perfumery and contains bornyl isovalerate, formate, butyrate, and acetate associated with sesquiterpenes; it is yellowish-green in colour; soluble in alcohol and ether; sp. gr. 0.940 to 0.965. The unpleasant odour of the crude drug is due to the hydrolysis of the oil during the slow drying process. It is used in medicine as a carminative.

**VALERIC (VALERIANIC) ACID** ( $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ ) — A colourless, oily acid of the fatty series which bears a similar relation to amyl alcohol as acetic acid to ethyl alcohol. It is of unpleasant odour and is said to exist in four different modifications, the normal variety being a liquid which boils at  $187^\circ\text{C}$ ., and is soluble in alcohol and ether. Iso-valeric acid ( $(\text{CH}_3)_2\text{CHCH}_2\text{COOH}$ ) is of boiling-point  $176^\circ\text{C}$ . One of the varieties is found naturally in many plants, particularly valerian root (see Valerian) and in angelica root from which it is obtained by boiling with soda. Valeric acid is a frequent product of the oxidation of the higher fatty acids, and can be prepared by the oxidation of amyl alcohol. It is used in medicine and perfumery.

**VALONIA** — Acorn cups and beards of the *Quercus ægilops*, *Q. robur*, and *Q. suber*, rich in tannin; grown in Asia Minor, Turkey, France, Greece, and Rumania, and used for tanning. Good qualities contain about 30 per cent., while Messenia valonia is stated to contain the highest percentage of tannin. An extract containing 64 per cent. tannin is prepared in Smyrna, and other extracts are commercially available.

**VANADINITE** — Mineral chlorovanadate of lead, of crystal system No. 3, and sp. gr. 6.6 to 7.0. (See Vanadium.)

**VANADIUM (V) and its Compounds** — Atomic weight, 50.95. See Elements for other data. Vanadium is a somewhat rare metallic element which occurs in the minerals *endlichite* or *vanadinite* (lead combination) ( $9\text{PbO}, 3\text{V}_2\text{O}_5, \text{PbCl}_2$ ), *pucherite* (a bismuth combination), *mottramite* (a lead and copper combination), *patronite* (an impure vanadium sulphide mined at Mina Ragra in Peru), *roscoelite* (a silicate), *sincosite* (a vanadium mineral found in Peru) ( $\text{V}_2\text{O}_4, \text{CaO}, \text{P}_2\text{O}_5, \text{H}_2\text{O}$ ), and *carnotite* (a potassium uranyl vanadate). It is also found present in Bessemer slag at times, being derived from certain iron ores in which it occurs naturally in small amount. Roasting the slag 5 to 8 hours at  $750$  to  $825^\circ\text{C}$ . with 20 per cent. of sodium chloride and a little lime converts 75 to 80 per cent. of the vanadium into soluble sodium metavanadate. Vanadium is also reported as being recoverable from the flue dust of certain petroleum fuel oils, specifically Venezuelan. The chief source of the metal lies in the Peruvian Andes and S.W. Africa.

Vanadium is recovered as oxide from the sulphide present in the mixture of *patronite* and asphaltic material found at Mina Ragra in Peru, by roasting the ore with a little added coal; the vanadium passes into the slag, which is granulated in water, dried, and reduced to ferrovanadium in a shaft furnace. Another method consists in roasting the ore with salt, thus producing sodium vanadate, which can be separated by solution in water, and then treated with hydrogen sulphide, the precipitated sulphide thus produced being subsequently reduced to oxide or to the metallic state, the latter being obtained by reduction of the oxide with carbon or aluminium powder in an electric furnace.

Carnotite ranks next in importance to *patronite* as the most important ore for vanadium. It is a yellow radioactive mineral of varying composition, containing uranium also, in association with lime and potash, and found in sandstone beds in the south-western part of Colorado and the south-eastern part of Utah. (See Radium.)

By roasting *roscoelite* with salt and pyrites, and subsequent leaching with hot water, sodium vanadate is obtained in solution, and by adding ferrous sulphate when cold, iron vanadate is precipitated.

Vanadium is of importance in the manufacture of certain kinds of steel, a very small proportion—little more than from 0.05 to  $\frac{1}{2}$  per cent.—removing occluded oxygen and nitrogen, and contributing tensile strength, elastic limit, and special properties of much value for particular applications; it also finds use as a catalyst in various processes, being less susceptible to catalytic poisoning than platinum. The oxidation of sulphur dioxide and oxygen to form sulphur trioxide uses vanadium pentoxide as catalyst, and it is similarly used in the oxidation of naphthalene and benzene with air to phthalic acid and maleic acid respectively. The metal is white, lustrous, harder than quartz, soluble in strong acids, and when heated in air burns brilliantly, forming the pentoxide ( $\text{V}_2\text{O}_5$ ) (sometimes called vanadic acid), a purple-coloured body almost insoluble in water but soluble in acids and alkalis, and used as a photographic developer, and, as stated above, as a catalyst.

## VANADIUM ORE AND CONCENTRATES, WORLD PRODUCTION

Annual average for the three-year period 1937-1939

Data arranged and rounded off by the Editor.

Country				Vanadium Ore and Concentrates as V Content Metric Tons	
U.S.A.	..	..	..	710	
Mexico	..	..	..	110	
				—	820
Peru	..	..	..		800
South-West Africa			..	550	
Northern Rhodesia			..	330	
				—	880
Sum of above	..	..	..		2,500

Germany produced vanadium, probably from the "minette" iron ores (0.1 per cent. V) of Luxembourg and Belgium, with a recovery of 50 to 60 per cent. of the vanadium content of the ore. See J. H. Fry, "General Review of German Metallurgical Practice," *Metal Progress*, 49, Jan. 1946, pp. 76-86; J. P. Gill, "German Toolsteel and Special Steel Industry," *Metal Progress*, 49, Jan. 1946, pp. 122-4, and *Steel*, 117, Sept. 24, 1945, pp. 120-36.

In the United States the principal source of vanadium is the sandstones of Colorado, Utah, and New Mexico. Additional sources are phosphate rock, and the flue dust and ash from oil-burning ships using Venezuelan oil.

Vanadium forms four **oxides**, namely, the pentoxide ( $V_2O_5$ ), mentioned above; the tetroxide ( $V_2O_4$ ), a blue, infusible solid; the trioxide ( $V_2O_3$ ), a black, infusible solid; and the dioxide ( $V_2O_2$ ), a light grey solid that ignites when heated in air; the oxides are insoluble in water, and used in metallurgy.

There are also three **chlorides**, namely, the tetrachloride ( $VCl_4$ ), a red liquid, of b.p.  $148^\circ C$ .; the trichloride ( $VCl_3$ ), a pink solid; and the dichloride ( $VCl_2$ ), a green solid; all three chlorides are soluble in water. The tetrachloride is used as a mordant in the textile industry.

Vanadium also forms a **carbide** (VC) (see Abrasives); a **nitride** (VN); and a **sulphate** ( $VSO_4 \cdot 7H_2O$ ), used as a mordant. Salts are known corresponding to the three unknown acids  $HVO_3$ ,  $H_3VO_4$ , and  $H_4V_2O_7$ . Complex vanadium **silicates** are used in place of platinum as catalytic agents, among other applications, for conversion of  $SO_2$  into  $SO_3$  in oleum manufacture.

(See *Strategic Minerals*, by J. B. De Mille (McGraw-Hill Book Co., New York); *Rarer Metals*, by J. B. DeMent and H. C. Dake (Chemical Publishing Co., Brooklyn).)

**VANDYKE BROWN** — Indefinite mixtures of iron oxide and organic matter, forming the constituents of bog-earth or certain natural ochres, and used as pigments.

**VANDYKE RED** is a pigment composed of a double cyanide of copper and iron ( $\text{Cu}_2\text{Fe}(\text{CN})_6$ ).

**VANILLA** — The pods of *Vanilla planifolia* and other species of an orchid which grows wild in Mexico, Brazil, and Guiana, and is cultivated in many tropical countries; the West Indies, the French colonies of Madagascar, Réunion, Comoro Islands, and the Seychelles furnishing the principal supplies. The pods contain shining crystals of vanillin ( $\text{C}_6\text{H}_3(\text{OH})(\text{OCH}_3)\text{CHO}$ ) in association with a resinous body and other constituents, and have a pleasant aromatic taste and odour.

The most suitable solvent for extracting vanilla from the beans is stated to be 65 per cent. ethyl alcohol. It is soluble in water, alcohol, and ether, has m.p.  $81^\circ\text{C}$ . and b.p.  $285^\circ\text{C}$ . Acetanilide is a common adulterant, and piperonal is also used at times.

Vanillin is largely used in perfumery, also for flavouring purposes, and in medicine. It is prepared on a large scale from coniferin ( $\text{C}_{16}\text{H}_{22}\text{O}_8, 2\text{H}_2\text{O}$ ), which by hydrolysis yields glucose and coniferyl alcohol ( $\text{C}_6\text{H}_3(\text{OH})(\text{OCH}_3)(\text{C}_3\text{H}_4.\text{OH})$ ), and the latter by oxidation gives vanillin. It is also obtained by the oxidation of eugenol, or preferably iso-eugenol (into which it is converted by heating with solid caustic potash), ozone being one of the agents employed. Further, it can be obtained from narcotine and cinnamic aldehyde and synthesized from protocatechuic aldehyde, and from guaiacol. There is also a process for its preparation from "sulphite lye" based on the lignin content of the lye (Kurschner).

**VAPORIZATION** — Passage from liquid to vapour form. (See Evaporation, and Vapour Pressure.)

**VAPOUR DENSITIES** — The relative weights of gases at the same temperature and pressure compared with hydrogen as the unit, determined either by ascertaining the weight of a given volume or the volume of a given weight of vapour. These densities are in some cases (including hydrogen, oxygen, nitrogen, chlorine, bromine, iodine) identical with their atomic weights. The principal exceptions are mercury, cadmium, zinc, potassium, sodium, arsenic, phosphorus, sulphur, and the rare gases.

The most general rule is that the vapour densities of the elements are one-half of their molecular weights, and the explanation of the above-noted exceptions is that the molecules of mercury, cadmium, zinc, potassium, and sodium consist of but one atom, so that their atomic and molecular weights are identical, while arsenic and phosphorus contain each four atoms in their molecules, and their smallest part that can take part in a chemical change is one-fourth of their molecular weights or one-half of their densities. (See Gases, Molecules, and Valencies.)

**VAPOUR PRESSURE** — When a dish of water is left exposed to the air the water slowly disappears and it is said that it evaporates. Furthermore, it is common knowledge that a given amount of water will evaporate more quickly on a warm day than on a cool day. If we

want to evaporate water still more quickly we heat it to boiling. If the same amount of water is placed in a shallow dish and in a tall cylinder and they are placed side by side so that the temperature of each is the same we find that the water in the container with the greater exposed area evaporates more quickly. Again, if equal amounts of ethyl ether, alcohol, and water are placed in three identical containers side by side we note that the ether disappears first, the alcohol next, and the water last.

From the above observations it becomes apparent that for a given liquid the temperature and the exposed surface area are factors in the rate of evaporation, whereas some liquids are more volatile than others when at the same temperature and with the same exposed area.

If one takes several glass tubes (lower end closed, and each more than 30 inches long) and completely fills each with mercury, then inverts them (while the open end is temporarily closed) in a vessel of mercury thereupon removing the closure, there is an empty space (Torricellian vacuum) above the column of mercury. If one tube is retained for reference, and into the others a few drops of (a) water, (b) ethyl alcohol, (c) ethyl ether is introduced (into each tube a single one of these liquids), the level of the mercury drops, at 25° C. (a) 24 mm. in the case of water, (b) 59 mm. for alcohol, (c) 537 mm. for the ethyl ether. These are the actual values of the vapour pressure of these liquids at the specified temperature, namely, 25° C.

Further experimentation shows that if the cross-sectional area of the tubes is varied the depression remains the same. As long as there is excess liquid present the vapour pressure of the liquid is a characteristic of the liquid at a given temperature.

In order to explain and understand this phenomenon, visualize a liquid as being made up of many small spheres (molecules) in turbulent motion, being attracted to each other by cohesive forces, yet undergoing elastic bombardment upon collision. A molecule *inside* the liquid will, in general, be acted upon by uniform attractive forces acting in all directions. On the other hand, a molecule *in the surface* will not have uniform forces acting upon it because it will have greater attraction on the side into the liquid than on the side away from the liquid. This will cause the surface layer to act like a membrane on the liquid (surface tension), tending to prevent the liquid molecules from escaping and becoming a vapour.

Due to the turbulent motion (kinetic energy) of the liquid molecules they will continually be undergoing elastic bombardment. The velocity of any single molecule at any instant can vary from zero to infinity depending upon its immediate past history. For example, consider two identical molecules travelling in opposite directions and colliding in a head-on elastic impact. At the instant of impact their velocities will be reduced to zero, however, since the impact was elastic the molecules will regain their former velocity although they will travel in opposite directions. Suppose there are two molecules travelling in the same general direction but at a small angle to each other so that after collision the velocity of one molecule is greatly

increased over its former velocity while the other molecule will be moving slower (the total kinetic energy of the two molecules is equal to what it was before collision). It is thus conceivable that by a series of favourable collisions a molecule can gain enough energy to break through the surface and maintain itself as a gaseous molecule—thus a liquid can change to a vapour, that is, evaporate. The energy removed from the liquid in the loss of a fast-moving molecule is restored by absorption of heat from the surroundings.

In an open container these vapour molecules can diffuse into the surrounding gases and thus entirely escape, other liquid molecules will do likewise until all the liquid disappears. As the temperature of the liquid rises the kinetic energy of the molecules increases and more will be able to break through the surface in a given time, thus increasing the rate of evaporation. Since evaporation is the escape of liquid molecules through the surface to form vapour molecules, it becomes apparent that the rate of evaporation will be proportional to the exposed surface area for a given liquid.

The cohesive or attraction forces of molecules of different liquids are different; therefore, at a given temperature, different liquids will have different abilities to break through their surface layers and go into the vapour phase. Thus the rate of evaporation of different liquids varies at the same temperature.

When a liquid is placed in a confined space some of its molecules tend to escape into the vapour phase due to their kinetic energy. The vapour molecules have the properties of a gas, that is, to fill all available space.

As the number of vapour molecules increases in a confined space many of them go back into the liquid surface and become liquid. After a time the rate of liquid molecules escaping into the vapour phase will be equal to the rate of vapour molecules condensing into the liquid phase; that is, there will be a state of dynamic equilibrium established. The molecules in the vapour phase, because of their kinetic energy, bombard the sides of the container and thus create a pressure. The equilibrium pressure between a liquid and its vapour in a closed container at a given temperature is called the vapour pressure of the liquid.

It should be pointed out that for a given liquid this pressure is a function of the temperature only and is not dependent upon the surface area, because equilibrium conditions exist and time is not a factor. Since the surface energy of liquids is characteristic for each liquid and since temperature is indicative of the kinetic energy of systems, it is not surprising to find that at a given temperature different liquids exhibit their own characteristic vapour pressures.

Table I shows the vapour pressures of some common liquids at different temperatures. The temperature at which the vapour pressure of the liquid becomes equal to 760 mm. of mercury pressure is the normal boiling point of the liquid.

If liquid  $\text{CO}_2$  is sealed in a high-pressure tube at  $20^\circ\text{C}$ . there is a definite line of demarcation (meniscus) between the liquid and the

vapour phases, furthermore, the density of the vapour is less than that of the liquid. If the tube is warmed up no visual change occurs until the temperature becomes  $31.1^{\circ}\text{C}$ . (which is far in excess of the normal boiling temperature); at this temperature the meniscus becomes vague and disappears. The density of the liquid and vapour phase becomes identical,  $0.460\text{ gm./c.c.}$ , and the pressure exerted on the walls of the tube is large,  $73.0\text{ atm}$ . The carbon dioxide under these conditions is said to be in its critical state and the corresponding conditions are known, respectively, as the critical temperature, the critical density, and the critical pressure.

TABLE I

## VAPOUR PRESSURE OF LIQUIDS IN MILLIMETRES OF MERCURY

Temp. °C.	Water	Ethyl Alcohol	Ethyl Acetate	Acetone	Ethyl Ether
0	4.58	12.2	24.2	115.6	185.3
10	9.21	23.6	42.8	184.8	291.7
20	17.54	43.9	72.8	285.7	442.2
30	31.82	78.8	118.7	421.5	647.3
40	55.32	135.3	186.3	612.6	921.3
50	92.51	222.2	282.3	860.6	1277.0
60	149.4	352.7	415.7	1190.0	
70	233.7	542.5	596.3		
80	355.1	812.6	832.8		
90	525.8	1187.0	1130.0		
100	760.0		1520.0		
Boiling points	$100^{\circ}\text{C}$ .	$78.3^{\circ}\text{C}$ .	$77.1^{\circ}\text{C}$ .	$56.1^{\circ}\text{C}$ .	$34.6^{\circ}\text{C}$ .

As implied by the experiment the critical temperature is that temperature above which a vapour (gas) cannot be liquefied by pressure alone. The critical temperature is a condition above which the molecules have so much energy the attractive forces between molecules cannot become effective and thus the vapour cannot become a liquid. (See Matter.)

When the pressure of water vapour in the air is less than that in equilibrium with the freezing liquid (ice-water-vapour), namely,  $4.6\text{ mm.}$ , and the temperature is reduced sufficiently, the vapour will condense directly into the solid state without forming liquid as an intermediate stage. When this condition exists in nature we have the formation of hoar frost or snow. On the other hand, if the vapour pressure of water vapour in the atmosphere is greater than  $4.6\text{ mm.}$  liquid water will form on cooling until the vapour pressure is reduced below the vapour pressure of the freezing liquid.

For long periods in the winter when the temperature does not rise above the freezing point of water, thin sheets of ice are observed to evaporate, that is, to change directly from the solid state into the vapour state. "Dry ice" (solid  $\text{CO}_2$ ) changes directly from the solid phase to the vapour phase at atmospheric pressure. The direct change of a

vapour phase into a solid phase and the reverse change without the intermediate liquid phase is called *sublimation*. Many substances can be purified by condensing their vapours below the freezing point of the substance, such as iodine, zinc, naphthalene, benzoic acid, sulphur, violet phosphorus, and grey arsenic.

Water can be cooled by placing it in a canvas bag and hanging it where the water seeping through the bag can evaporate quickly. This method is used extensively in many parts of the world. The cooling effect of water upon the atmosphere is well known. These phenomena are a result of the large quantity of energy that must be absorbed in changing a liquid into the vapour phase without changing the temperature. Thus when water evaporates from the surface of a canvas bag part of the energy for the evaporation comes from the water in the bag, causing it to become cooler. The amount of heat necessary to change unit weight of liquid into unit weight of vapour without changing the temperature is known as the **heat of vaporization**. Thus it requires 539.55 calories to change one gram of *liquid water* at 100° C. into one gram of *water vapour* at 100° C. The heat of vaporization for ammonia is 301.6 cal./gm. at 0° C.; carbon dioxide is 55.0 cal./gm. at 0° C.; hydrogen sulphide is 131.9 cal./gm. at -61.4° C.; and oxygen is 50.9 cal./gm. at -182.9° C.

It requires more energy to convert one gram of water at 40 degrees into vapour at 40 degrees than it does to convert one gram of water at 100° C. into vapour at 100° C. The heat of vaporization for water at various temperatures is given in Table II.

TABLE II  
HEAT OF VAPORIZATION OF WATER

Temperature ° C.	Calories per Gram at 15° C.
0	595.9
20	584.9
40	574.0
60	563.2
80	551.7
100	539.6
120	525.7
140	511.1

Whenever there is a change of state, energy will be either absorbed or evolved, depending upon whether the final phase has more energy than the initial phase. Thus 539.55 calories of heat per gram of water will be absorbed when liquid water at 100° C. is changed into water vapour (steam) at 100° C. and 539.55 calories of heat per gram of steam is evolved upon condensing the steam into water at 100° C. Similarly, the **heat of fusion** of water, namely, 79.71 calories per gram of water at 0° C., is the number of calories evolved per gram of water to change it into one gram of ice, both ice and water being at zero degrees Centigrade. Also, the **heat of sublimation** of ice is the

number of calories absorbed when one gram of ice changes into one gram of vapour, both being at the same temperature. Whenever one gram of a solid changes its crystalline structure a **heat of transition** accompanies the change; that is, when one gram of rhombic sulphur changes into monoclinic sulphur a definite amount of heat is always associated with the change.

The heat associated with any of the above changes is characteristic for each substance.

*References:* "Temperatures Below One Degree Absolute," by Giauque (*Ind. Eng. Chem.*, **28**, 743 (1936)); *Textbook of Physical Chemistry*, by S. Glasstone (D. Van Nostrand Co., New York).

**VAREC (Varech)** — The Normandy name for the ashes of sea-weeds. (See Barilla, Iodine, Kelp, Sea-Weeds, and Vriac.)

**VARISCITE** — A mineral form of hydrated aluminium phosphate ( $\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$ ).

**VARNISHES** are solutions of resinous substances which, when spread over the surface of any object, leave behind, after evaporation of the volatile vehicle, a thin shiny layer of the dissolved bodies, and are used as protective coverings to painted wooden, iron, and other surfaces. Animé, asphalt, benzoin, copal, dammar, elimi, mastic, resin, sandarac, shellac, etc., are all used in compounding them according to the purpose of their applications, copal varnish being one of the most important. Common resin cannot be used in its original state, but is first softened by heating with lime out of contact with air, or is esterified with glycerine.

To dissolve copal and some of the other resins or gums which are practically insoluble, it is requisite to powder and subject them to a process of dry distillation (or so-called "gum-running") at a temperature of about  $360^\circ\text{C}$ ., by which treatment they lose from 20 to 25 per cent. of their weight, but in this viscous condition can then be dissolved in turpentine and boiled or blown linseed oil. While these two liquids are used in compounding ordinary varnishes, other kinds are made using alcohol, petrol, turpentine, or other solvent alone or in admixture.

For the removal of impurities in suspension in ordinary varnishes (fluids of extreme viscosity) resort is had to deposition or, better still, to the use of centrifugal force, one appliance used for the purpose being the Sharples "supercentrifuge," the deposited matter being known as "foots." The same treatment gives good results for the removal of mucilage from linseed oil intended for use in varnish-making.

**Driers** are chemical materials used in oil-boiling, varnish and paint-making to facilitate the drying of the final products, and are introduced after making the varnishes and churned in. For varnish-making, manganese dioxide, cobalt and manganese resinates, oleates and borates, litharge (lead oxide) and zinc sulphate are used among others; while for paints, apart from the drying properties of any lead oxides that may be incorporated, and that of the varnish itself (when incorporated in the paints), the drying depends mainly upon the boiled or blown linseed oil used in compounding them. Driers modify the

course of oxidation, the oxygen absorption being lower than that observed when they are absent, while the amount of carbon dioxide evolved is approximately the same. It is therefore concluded that driers do not act as true catalysts. The maturing of varnishes takes time, and while cheap qualities are ready in certain cases to draw off from the "foots" within a year, others of higher quality call for storage over a number of years and in certain cases subsequent filtration through a filter press.

Vanadium driers are stated to be little less efficient than cobalt driers and act much more rapidly in the initial oxidation of linseed oil than lead driers; the rapid absorption of oxygen continues for much longer, about 1.75 times as much oxygen being absorbed. (See "A Century of Progress in Driers," by A. C. Elm (*Ind. Eng. Chem.*, **26**, 386 (1934)).)

Asphalt (bitumen) is largely used in making black varnishes, and "Albertol" and other synthetic resins and other compounds have come into considerable use in the preparation of various varnishes.

Insulating varnishes for coils of electrical transformers are made from a base commonly compounded of Chinese wood oil (tung oil), linseed oil, and suitable resins or ester gums, the solvents used being the higher gravity petroleum fractions or the lower ones with an added proportion of benzene. Silicone (see same) varnishes show excellent electrical insulating properties.

**Spirit Varnishes** consist of gum shellac or other resin dissolved in a suitable volatile solvent or mixture of solvents according to the nature of the application to be made of the products, pigments being introduced at times, and proportions of pyroxylin being sometimes substituted for the shellac or resin.

With respect to the **blooming** of varnishes, investigations have shown that bloom is of two forms, one being a crystalline deposit of ammonium sulphate obtained from the air, and the other a deformity of the surface brought about by certain conditions.

*References: Volatile Solvents and Thinners Used in the Paint and Varnish Trades*, by N. Heaton (Ernest Benn, London); *Natural Varnish Resins*, by T. H. Barry (Ernest Benn, London); *Varnishes and their Contents*, by R. S. Morrell (Oxford University Press, London); *Colours and Varnishes*, by Ch. Coffignier (Scott, Greenwood and Sons, London); *Cellulose Ester Varnishes*, by F. Sproxtton (Ernest Benn, London); *Protective and Decorative Coatings*, by Joseph J. Mattiello, editor (John Wiley and Sons, New York, 5 volumes); also "Albertol," Dopes, Gums, Lacquers, Linseed Oil, Nitrocellulose, Paints, Plasticizers, Pyroxylin, Resins, and Silicones.

**"VASELINE"** — The trade mark of proprietary products consisting largely of petroleum jelly (which see).

**VAT DYESTUFFS** — See Dyes.

**VEGARD'S RULE** — A rule concerning mixtures, which states that the volume change of an ideal solid solution is proportional to the atomic percentage of the solute component.

## 1122      VEGETABLE BLACKS— VENTZKE DEGREES

**VEGETABLE BLACKS** — Carbon pigments from various sources. (See Bone Black, Carbon, Ivory Black, and Lamp Black.)

**VEGETABLE IVORY** (*Tagua* Nut) — The kernels of the *Phytelephas macrocarpa* tree which grows in Peru, Colombia, and other parts of South America. The substance of these nuts has the appearance of ivory and is very hard, but can be turned in the lathe, and is used for making buttons, umbrella handles, and trinkets. By treatment with dilute sodium hydroxide it yields a substance named mannan, which is related to the cellulose group of chemical compounds. (See Mannose.)

**VEGETABLE OIL SEEDS** — See Oil Cakes.

**VEGETABLE OILS AND FATS** — See Fats and Oils.

**VEGETABLE TALLOW** (*Chinese*)—The white waxy substance found as a covering on the fruit of *Stillingia seberifa* (N.O. Euphorbiaceæ), cultivated in Hupeh, Szechwan, Hunan, Kiangsi, and Kweichow provinces, also Japan. The tallow tree is described otherwise as a member of the Spurge family (*Sapium sebiferum*) and is said to grow to a height of from 40 to 50 feet. The tallow of the "prima" quality has a m.p. of 36° to 47° C., sp. gr. 0.884 to 0.904, sap. v. 206, i.v. 19.4 to 60.8, and is used for candle and soap making.

The pale yellow oil expressed from the seeds, after steaming them to remove the exterior fat, amounts to about 19.2 per cent.; it is known locally as *ting-yu*, or *tze yu*, has an odour like that of linseed oil, and constitutes the *Stillingia* oil of commerce, having a sp. gr. of about 0.873, sap. v. about 200, and i.v. about 160. The component fatty acids are chiefly palmitic 57 to 69 per cent. and oleic 21 to 34 per cent.

The so-called "secunda" vegetable tallow is the mixture obtained from the seeds without first removing the exterior tallow, and, like the tallow, is used for candle and soap making, also as a lubricant and for dressing textiles in common with the *Stillingia* oil. Various mixtures are offered commercially, and it is stated that other varieties of fat are extracted from the trunk and bark of the trees, known as *o'chia*.

The refuse of the seed is said to be a valuable tobacco-plant manure, while the bark of the tree is used in medicine, and the leaves furnish a black dye.

**VEGETABLE WAX** (*Japan Wax*) — See Waxes.

**VENETIAN RED** — A pigment and polishing-powder, consisting of ferric oxide, made from red hematite or by calcining ferrous sulphate.

**VENICE TURPENTINE** — See Turpentine.

**VENTZKE DEGREES** are referable to a determination of the sucrose or cane-sugar content of a solution made by means of a polariscope, the scale being so graduated that the amount is read off direct. When the normal weight of 26.048 grams of sucrose is dissolved in 100 c.c. of solution in a 200 mm. tube, the degree registered is 100 and so on.

**VERATRINE (Cevadine)** — This is really a mixture of alkaloids, obtained by extraction with alcohol, from sabadilla (cevadilla), the dried ripe powdered seeds of *Schænocaulon officinale*, growing in Mexico, Guatemala, and Venezuela. The chief alkaloid is cevadine ( $C_{32}H_{49}O_9N$ ) (veratrine) of m.p.  $205^{\circ}C.$ , readily soluble in alcohol, and it is accompanied by veratridine ( $C_{29}H_{51}O_8N$ ), cevadilline ( $C_{34}H_{53}O_8N$ ), sabadine ( $C_{29}H_{51}O_8N$ ), and cevine ( $C_{27}H_{43}O_8N$ ). Extremely poisonous and seldom used in medicine. (See Sabadilla.)

**VERATRUM** — The dried rhizome and roots of *Veratrum viridis*. Used in medicine. (See Delphinine, and Hellebore.)

**VERBENA OIL** — The volatile oil distilled from the leaves of *Lippia citriodora*, cultivated in Spain and Southern France. It contains from 20 to 38 per cent. of citral, together with linalyl acetate, geraniol and *l*-limonene; soluble in alcohol and ether; opt. rot.  $-8^{\circ}$  to  $-16^{\circ}$  at  $20^{\circ}C.$ ; sp. gr. 0.900 to 0.918 at  $15^{\circ}C.$ ; used in perfumery and as a flavouring agent. Oil of lemon grass is also known as Indian oil of verbena but is not to be confused with the genuine verbena oil, which possesses a more delicate odour. (See Citronella Oil, Lemon Grass Oil.)

**VERDIGRIS** — See Copper.

**VERJUICE** — See Vinegar.

**VERMICULITE (Ferrous Aluminium Magnesium Silicate)** — A micaceous alteration product of the mineral biotite. It expands upon rapid heating, with accompanying expulsion of water of constitution, leaving a residual material of high heat insulation value that is comparable in this respect to asbestos corrugated board. The density of the commercially prepared material is about 8 pounds per cubic foot. Approximately 50,000 tons per year is produced in the U.S.A., and 1,000 in the Union of South Africa.

**VERMIFUGES** — See Insecticides.

**VERMILION** — The manufacture of this compound is a notable industry in Hong Kong, the article being used by the Chinese in varnish-making, for colouring candles and paper, and for stamping and writing purposes. (See Cinnabar, and Mercury (Sulphide).)

**VERMILION SUBSTITUTE** — A preparation which has largely supplanted mercuric sulphide, consisting of about 95 per cent. red-lead ( $Pb_3O_4$ ) coloured with eosin (tetrabromofluorescein,  $C_{20}H_8O_5Br_4$ ) — a red, crystalline, organic dye. (See Eosin.)

**VERMOUTH** — An alcoholic beverage with a basis of white wine. The Italian variety is made from super alcoholized muscatel wine, sweetened with sugar, to which wormwood, gentian, and extracts of other bitter herbs are added to lend special flavour; while the French product is similarly made, using the driest white wine that is procurable. (See Absinthe, and Wormwood.)

**"VERONAL"** — See Barbitone.

**VESUVIAN (Vesuvianite, Idocrase)** — A crystalline mineral varying in colour from brown to green, consisting in the main of calcium aluminium silicate, occurring in dolomitic rocks, limestone, serpentine, gneiss, etc. ; crystal system No. 2, and sp. gr. about 3.4.

**VETIVER OIL (Vetivert Oil, Cuscut Oil)** — A volatile oil distilled from the roots of the cuscus grass, *Vetiveria zizanioides*, which occurs wild throughout India, Ceylon, Brazil, and the West Indies. It is a thick yellowish-brown oil of violet-like odour, containing a sesquiterpene, vetivene,  $C_{15}H_{24}$ , and an alcohol vetivenol,  $C_{15}H_{26}O$  ; soluble in alcohol and ether ; sp. gr. about 1.000 to 1.030 at  $15^{\circ}C.$  ; opt. rot.  $+25^{\circ}$  to  $+38^{\circ}$  at  $20^{\circ}C.$  ; ref. ind. 1.517 to 1.520 at  $20^{\circ}C.$  Used in perfumery.

**"VIBRAC"** — A nickel chrome steel of exceptional strength, said to have the property of never tempering brittle, of great elastic limit, very consistent, and largely adopted for aeroplane and automobile work.

**VINASSE** — The residue left after fermentation of beet molasses, containing potassium salts and some nitrogenous matter, which qualify it for use both as a fertilizer and cattle food. (See Molasses, and Sugar.)

**VINEGAR** is a preparation of acetic acid, of which it contains a legal minimum of 4 per cent. The ordinary English variety is made, in part, by the method referred to under Acetic Acid, and otherwise as described below under Malt Vinegar, the British production being estimated at 25 million gallons per annum. In Germany and France it is made from wine by exposure to the air in casks containing some beech-shavings or by mere exposure to the air in sunlight ; in the United States cider or apple vinegar is preferred. Orange juice can also be employed, in which case the product contains some citric acid. Small proportions of alcohol and furfural are found present at times. All are made from alcoholic liquids by agency of certain organisms (or their enzymes), including the *Bacterium aceti*, *B. Pasteurianum*, *B. xylinus*, *B. Kulzingianum*, and *B. Acetigenus*. (See *Vinegar: Its Manufacture and Examination*, by A. Ainsworth Mitchell (C. Griffin and Co., London) ; Acetic Acid, and Pyroligneous Acid.)

**Malt Vinegar** is prepared from malt or malt and raw barley mashed as in brewing, and then submitted to vinous fermentation and subsequently soured as already described.

**Distilled Vinegar** is any variety of vinegar submitted to distillation, so that it is thereby deprived of its colouring matter.

**Balsam Vinegar** — So-named "Balsam" vinegar was originally made from a mixture of strong must from the white Trebbiano grape with strong ordinary vinegar by storage in wooden casks for many years up to a century. A fairly good balsam vinegar is now made by adding old vinegar to boiled must.

**Banana Vinegar** is made from the pulp and peel of the ripe fruit containing some 16 per cent. fermentable sugars. The mash is pasteurized at  $75^{\circ}C.$  for forty-five minutes and inoculated when cold with *Saccharomyces ellipsoideus*, etc.

**Tomato Vinegar** is vinegar flavoured with an infusion of tomatoes, or tomatoes may be added to the alcohol or wine before acetification.

**Verjuice** is vinegar made variously from the juices of crab apples, unripe grapes, and sour cider.

**VINYL ALCOHOL**—See "Elvaol."

**VINYL ETHERS**—See Ethers.

**VINYL RESINS**—These are formed by the polymerization of vinyl compounds such as chloride, alcohol, acetate, ether, ketone and acetal, by the action of catalysts or ultra-violet light. These resins are colourless, odourless, tasteless, non-inflammable; may be coloured any shade with dyes or pigments; are transparent when pure, and any degree of opacity may be obtained by the incorporation of fillers. They may be moulded, sheeted, or extruded, and are thus used to impregnate textiles or paper, and for dentures, phonograph records, and building construction.

Properties: moulding pressures, 1,200–1,800 lb. per sq. in.; moulding temperatures, 115–130° C.; tensile strength, 8,000–10,000 lb. per sq. in.; specific gravity, 1.35; softening point, 50–65° C.; dielectric strength, instantaneous, 400–500 volts per mil. at 25° C.; Brinell hardness number, 10.0–15.0 (550 lb.-3 min.). See J. G. Davidson and H. B. McClure (*Ind. Eng. Chem.*, **25**, 645 (1933)); G. O. Curme, Jr., and S. D. Douglas on "Resinous Derivatives of Vinyl Alcohol" (*Ind. Eng. Chem.*, **28**, 1123 (1936)); K. G. Blaikie and R. N. Crozier on "Polymerization of Vinyl Acetate" (*Ind. Eng. Chem.*, **28**, 1155 (1936)); and Plastics.

**"VINYLITE"**—Trade-mark for vinyl and polyvinyl synthetic resins and plastics. (See Vinyl Resins, and Gums and Resins (Synthetic).)

**VIOLET ESSENCE**—See Ionone, and Orris Oil.

**VIRUSES**—See Bacteria.

**VISCOGEN**—Calcium saccharate. (See Sugar).

**VISCOID**—See Silk Substitutes.

**VISCOSE**—A plastic prepared from cellulose by dissolving it in alkali (18 per cent. strength of NaOH) and carbon disulphide, and, after a period of ripening, reprecipitating the cellulose by extruding the solution, in the form of fibres and films, into dilute acid. After removal of the precipitated sulphur by treating with sulphide solution a product containing 85 to 90 per cent. cellulose is obtained. The fibres are called rayon, and the films cellophane. (See Silk Substitutes.).

**VISCOSIMETER (Viscometer)**—An apparatus for measuring the viscosity of fluids. (See Lubricants, Oils, and Viscosity.)

**VISCOSITY**—The term viscosity means the resistance shown by a fluid to flow, and it is measured by the tangential force per unit area of either of two horizontal planes at unit distance apart, one of the planes moving with unit velocity relative to the other, the space between being occupied with the flowing fluid (Maxwell).

The C.G.S. unit (centimetre-gram-second system of physical units) is that of a fluid in which the tangential force per sq. cm. exerted on each of two parallel planes 1 cm. apart in the fluid is one dyne, when one of the planes is moving with a velocity of 1 cm. per second in its own plane relatively to the other.

In plain terms, the viscosity or resistance to flow of a colloid or a solution is ascertained by measuring the time of outflow from a standard volumetric pipette; roughly expressed, the viscosity is inversely proportional to that time. The viscosity of oils and greases, which, of course, largely depends upon the temperature, is determined in much the same way, or by the time taken, under standardized conditions, for a metallic bulb to fall through a measured column of the substance under examination.

Viscosity diminishes as temperature rises, and increases to some extent as pressure rises. The B.S.I. (B.E.S.A.) have issued a specification in respect of the determination of viscosity in absolute units. According to D. B. Macleod, the viscosity of liquids is inversely proportional to the free spaces within them, and is to be interpreted as a simple function of the molecular weight.

The effect of pressure on viscosity has been studied by R. B. Dow, M. R. Fenske, and H. E. Morgan (*Ind. Eng. Chem.*, **29**, 1078 (1937)), who report a nearly fifteen-fold increase of viscosity at 86° F. of "Aroclor 1254" over a pressure range of 3,500 pounds per square inch. The claim is made that this is "the greatest increase of viscosity that has been measured for any liquid."

The "Redwood," "Saybolt," and "Engler" viscometers are the best-known types for determinations of the one class, whilst the "Michell" viscometer shows advantages in respect of the other or "falling-ball" type. It is also reported that the "plastometer" (see Plastometer) and the "MacMichael" and "Doolittle" torsional viscometers are the only reliable instruments for determining the viscosities of varnishes. The "Stormer" and "Ostwald" viscometers are other types.

*References:* The relationship of viscosity and structure of 50 synthetic hydrocarbons, which are alkyl derivatives of benzene, naphthalene, diphenyl in *Ind. Eng. Chem.*, **28**, 972 (1936); "Viscosity and Chemical Constitution," by M. Souders, Jr. (*J. Amer. Chem. Soc.*, **60**, 154 (1938)); *A Monograph of Viscometry*, by Guy Barr (Oxford Univ. Press; Humphrey Milford, London); *The Viscosity of Liquids*, by E. Hatschek (G. Bell and Sons, London); *Viscometry*, by A. C. Merrington (Longmans, Green and Co., London and New York); and Lubricants.

**VITAMINS** — The term vitamin is used to designate a number of organic compounds which do not fall into the categories of the ordinary nutrients — proteins, fats, carbohydrates, and inorganic salts — but which, despite the minute quantities present in most natural food materials, are nevertheless essential for normal nutrition in animals and man. As the number of known vitamins increases, the legitimacy of the term becomes more questionable and the use of alternatives, such as "essential

metabolite" hardly solves the difficulty. So great is the output of literature in the vitamin field from the chemical, nutritional, and clinical aspects that any review of the subject quickly becomes out of date. Among books covering much of the field are *Chemistry and Physiology of the Vitamins*, by H. R. Rosenberg, Interscience Publishers, New York, 1942; *The Vitamins in Medicine*, by F. Bicknell and F. Prescott, Heinemann, London, 1942; *Plants and Vitamins*, by W. H. Schopfer, Chronica Botanica Co., Mass., U.S.A., 1943; and *Food and Planning*, by J. R. Marrack, Gollancz, London, 1943. *The Annual Reviews of Biochemistry*, Stanford University P.O., California, and the Biochemistry section of the *Annual Reports of the Progress of Chemistry*, of the Chemical Society, London, give good reviews of the literature to date.

As certain of the vitamins are essential for the development of various bacteria and mould fungi, such organisms are being increasingly used for the assay of the vitamins. Such techniques are far less time-consuming than bio-assays involving the use of animals.

**Vitamin A — General Properties** — Actually at least three separate vitamins;  $A_3$  has been recently isolated in pure form (Robeson and Baxter, *Nature*, **155**, 300, 1945). The three are closely related,  $A_3$  probably being an isomer of  $A_1$ ;  $A_2$  has not been isolated in the pure state, or separated from  $A_1$ . All three have similar properties, being fat soluble but water insoluble. They form pale yellow crystalline plates, are readily oxidized, but heat stable in the absence of air. They are destroyed by ultra-violet light.

**Functions** — The A vitamins or their provitamins seem to play a part in connection with the reproductive functions, which may be associated with their part in the stimulation of the building of cells. They are also concerned in the metabolism of carbohydrate and fat, but the most important function is their role in the production of visual purple, which is essential to the mechanism of sight in dim light.

**Results of Deficiency** — The most striking and first noticeable symptom is "night blindness." Another effect, apart from retarded growth, which is not specific to this vitamin, is the effect on epithelial tissue: in man, a dryness of the skin is a marked feature and the effect on the mucous membranes is to cause a degeneracy which lessens resistance to bacterial infection. Defective enamel deposition on the teeth is a further result.

**Hypervitaminosis** — Excessive doses are harmful to rats. No ill effects are known from over-doses of the A provitamins.

**Sources** — The A vitamins are derived from at least nine provitamins, carotenoids, which occur in plants, the conversion usually occurring in animals, principally in the liver. Animals can store large quantities of the vitamin. The chief sources of provitamins are carrots, lettuce, spinach, water-cress, green vegetables, eggs, liver, milk and milk products, and fish liver oils. The last named is the most important commercial source, and also yields considerable amounts of vitamin D. The vitamin is isolated by vacuum distillation or low temperature fractional distillation.

are discussed by C. C. Ungley in *Brit. Med. J.*, 2, 1370 (1949). (See "Anacobin," and "Cytamen.")

**Nicotinic Acid** — Also known as Niacin or P.P. (Pellagra preventive) factor.

**Properties** — Melts at 235 to 236° C. Sublimes without decomposition. Soluble in water and alcohol. Nicotinamide, the form in which the vitamin occurs in the body, crystallizes from benzene and melts at 129° C.

**Functions** — There are several nicotinamide-containing enzyme systems whose action is the dehydrogenation of various substrates. The nicotinamide part is responsible for the phenomenon of the reversible reduction-oxidation reaction of the cohydrogenases. Administration to diabetics results in improved carbohydrate tolerance.

**Results of Deficiency** — Causes black-tongue in dogs, and pellagra (lesions of the mucous membranes and of the skin): in later stages, mental disorders and lesions of the central nervous system.

**Hypervitaminosis** — Excess (over 100 mgm.) toxic, causes flushing and sickness.

**Sources** — Liver, yeast, wheat germ, meat.

**Synthesis** — By oxidation of nicotine or  $\beta$ -pyridines. By decomposition of pyridine-poly-carboxylic acids.

**Assay** — Colorimetrically—cyanogen-bromide method, or 2,4-dinitrochlorobenzene. Microbiologically, with *Lactobacillus arabinosus*.

**Standard** — No standard yet set up.

**Pyridoxin (Adermin)** — B<sub>6</sub>.

**Properties** — Melts at 160° C. Thermolabile. Soluble in water, alcohol, acetone (slightly soluble in ether and chloroform). Optically inactive. As hydrochloride (in which form it is marketed), stable to heat, hydrochloric acid, and alkali, but destroyed by light.

**Functions** — Probably connected with utilization of unsaturated fatty acids. The necessity of this vitamin for man has not been proved.

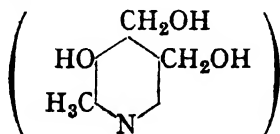
**Results of Deficiency** — Necessary for egg-production in pullets. Deficiency causes acrodynia in rats.

**Hypervitaminosis** — B<sub>6</sub> has a sedative effect in man.

**Sources** — Yeast, rice polishings, seeds, and cereals.

**Synthesis** — 1. By degradation of isoquinoline. 2. By complete synthesis, building up pyridine nucleus from small aliphatic molecules. 3. By diazotization of ethoxy-diamine to an ethoxy-dihydroxy compound which on hydrolysis with dilute HCl gives B<sub>6</sub>.

The formula of the resulting vitamin B<sub>6</sub> is 3-hydroxy-4, 5-di(hydroxymethyl)-2-methylpyridine



**Assay** — Biologically, by rat growth; colorimetrically; and micro-

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**Standard** — 1 rat unit = 10 $\gamma$ . This is defined as the daily amount necessary to prevent or cure symptoms of deficiency.

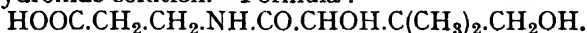
**Pantothenic Acid** — *General Properties* — Soluble in water, ethyl acetate, and glacial acetic acid; less soluble in ether and amyl alcohol. Sensitive to acids, bases, and heat. In pure form a pale yellow viscous oil. Dextrorotatory.

*Functions* — Role undetermined both in plants and animals. Human need not yet demonstrated.

*Results of Deficiency* — In rats, deficiency causes atrophy of hair bulbs and follicles, and cessation of melanin deposition, hence loss of hair colour. Chicks show specific dermatitis.

*Sources* — Yeast, liver, kidney, rice bran.

*Synthesis* — Condensation of a  $\beta$ -alanine ester with  $\alpha$ -hydroxy- $\beta\beta$ -dimethyl- $\gamma$ -butyrolactone, and saponification of the product with cold barium hydroxide solution. Formula:



*Assay* — Microbiologically with *Saccharomyces carlsbergensis*, or various bacteria. There are no specific chemical or physical tests known for pantothenic acid.

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**Inositol** — Bios I.

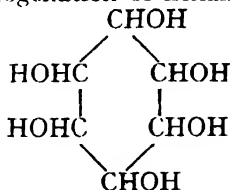
*General Properties* — Thermostable. Sweet taste. Soluble in water, but insoluble in ether and absolute alcohol. Crystallizes from acetic acid or water below 50° C. as the dihydrate, but above 50° C. as the anhydrous salt. Dihydrate melts at 215 to 216° C., anhydrous compound at 225 to 226° C.

*Functions* — The mechanism of the inositol action is not known, though it appears to act as a lipotropic factor. It markedly increases peristalsis of the stomach and small intestine, and stimulates growth of the intestinal bacteria.

*Results of Deficiency* — Development of fatty livers.

*Sources* — Citrus fruits, leaves, cereals, and yeast.

*Synthesis* — By hydrogenation of hexahydroxybenzene. Formula:



*Assay* — Best method is microbiological, by yeast growth. Biological method is by cure or prevention of alopecia in mice. No specific chemical method.

*Requirement* — Human requirements not established.

**Para-Aminobenzoic Acid** — *Properties* — Thermostable. Colourless substance, melting at 186 to 187° C. Water soluble.

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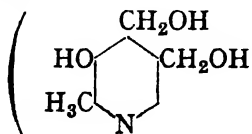
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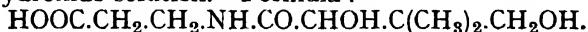
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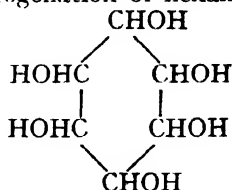
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*Requirement* — Human requirements not established.

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*Functions* — Probably acts by blocking certain enzyme systems.

Highly effective detoxicant for lethal doses of arsenicals. Necessary for growth of many bacteria.

*Results of Deficiency* — Retardation of growth in chicks. Produces greying of hair in rats.

*Sources* — Yeast.

*Assay* — Colorimetrically; microbiologically by growth of *Neurospora crassa* mutant; biologically by cure or prevention of achromotrichia in rats, or growth of chicks.

*Requirements* — Human requirements not yet known.

**Biotin** — Co-enzyme R, Vitamin H, Bios IIB.

*Properties* — Thermostable. Water soluble.

*Functions* — Necessary for good growth and reproduction in hamsters. High level in blood (of chicks and ducks) related to rapid elimination of malarial parasites.

*Results of Deficiency* — Not known.

*Source* — Yeast.

*Synthesis* — Recently achieved (*J. Amer. Chem. Soc.*, **66**, 1756, 1944).

*Assay* — Microbiologically, by growth of yeast or *Rhizobium* sp. This factor is inactivated by avidin (a constituent of raw egg white).

**Choline** — *Properties* — Colourless, strongly alkaline, very hygroscopic liquid. Absorbs CO<sub>2</sub> from the air. Soluble in water and alcohol, insoluble in ether.

*Functions* — Takes part in methylating action of the liver. Necessary for normal growth and lactation of rats. (After acetylation, choline in the body lowers the blood pressure.)

*Results of Deficiency* — Deposition of fat, and to a lesser extent of cholesterol esters, in liver of dogs and rats. Hæmorrhagic degeneration of kidneys. In chicks, decrease or cessation of egg production. Prolonged deficiency causes loss of ability of liver to store glycogen.

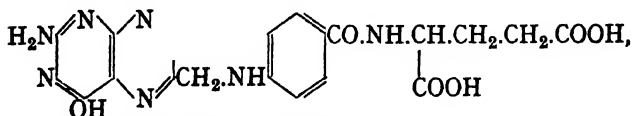
*Assay* — Microbiologically by growth of *Pneumococcus* sp.

It is doubtful if this is justifiably regarded as a vitamin: it is replaceable by methionine and betaine.

**Folic Acid** — *Properties* — Slightly soluble in water; orange-yellow in colour.

*Functions* — Seems to be essential for normoblastic blood formation in man. It is effective in restoring the blood count to normal, but has no effect on the neurological complications of pernicious anaemia. It is identical with vitamin B<sub>9</sub>, *Lactobacillus casei* factor, and *Streptococcus lactis* R factor, but not identical with the anti-pernicious anaemia factor in liver (see vitamin B<sub>12</sub>).

*Sources* — Liver, yeast, and green vegetables. It is also produced synthetically. Its formula is:



and name, pteroylglutamic acid.

**Assay** — Microbiological older method depending upon the growth of *Streptococcus Lactis R.* Colorimetric newer method depending upon reduction with zinc amalgam, diazotization, and final reduction with N-(1-naphthyl)-ethylenediamine.

#### INHIBITION BY B VITAMINS

*p*-Aminobenzoic acid counteracts the action of hydroquinone, sulphapyridine, and sulphanilamide, probably because it has a common point of attack on some enzyme system.

Pyrithiamin bears the same relationship to thiamin as sulphapyridine does to *p*-aminobenzoic acid; but its use as a chemotherapeutic agent is doubtful as non-toxic levels are not anti-bacterial to mice.

**Vitamin C (Ascorbic Acid)** — *Properties* — Colourless and odourless crystals melting at 192° C.; water soluble. Inactivated by oxidation, particularly at higher temperatures, but stable at ordinary temperatures if kept dry and not exposed to light. In solution, reasonably stable if kept in air-free containers. Oxidizes readily in presence of iron or copper, or of riboflavin (vitamin B<sub>2</sub>).

*Functions* — The formation of intercellular "cementing" substances, including bone and tooth formation, is best established function. It appears also to be connected with cellular respiration (where it acts as a hydrogen-transporter), and with carbohydrate and amino-acid metabolism. It may also be a factor in resisting infection. There is recent evidence of the vitamin being concerned in the reproductive functions of both male and female bovines, and in the mare. Necessary for normal healing of wounds. There is some evidence of a synergy between vitamins A and C in this matter, and in other respects between B and C.

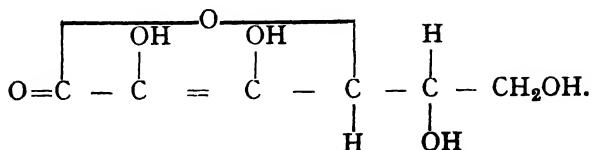
*Results of Deficiency* — Scurvy. Sore and swollen joints, œdema, hæmorrhage, fragility of bones, decay of teeth; in infants, Möller-Barlow's disease.

*Hypervitaminosis* — Unknown with this vitamin.

*Sources* — Widely distributed, the best sources being fresh fruits and plants, particularly rose hips, red and black currants, citrus fruits, strawberries, various cabbages, and pepper. Human milk contains an appreciable amount, as also does the liver of various animals and fish. Some animals, not including man, are able to synthesize ascorbic acid.

*Synthesis* — Isomerization and lactonization of 2- or 3-keto-hexonic acids is the chief method. Condensation of ethyl glyoxylate or ethyl mesoxylate with *l*-threose, or the ester condensation of benzoyl-glycolic acid with an  $\alpha$ -oxy acid are other syntheses.

The formula of the resulting vitamin C is



*Assay* — Biological, spectroscopic, and polarigraphic and a number of chemical methods are available. Of the last named the commonest are modifications of the titration method with 2,6-dichloro-phenol-indophenol.

*Standard* — 1 I.U. (International Unit)=0.05 mg. of pure ascorbic acid.

*Requirement* for human beings, 50 to 100 mg. daily. Infants need 3 to 8 mg. per kilogram of body weight.

**Vitamin D** — The antirachitic or "sunshine" vitamin. This is a group of substances of which the individual members have not been named, except D<sub>2</sub>, which is known as "calciferol" in England and "viosterol" in the United States; it is irradiated or activated ergosterol. The D vitamins are produced by the activation of certain D provitamins, such as ergosterol, which occur in plants and animals.

*General Properties* — The D provitamins, of which there are at least ten, are insoluble in water but soluble in organic solvents. The D vitamins are also insoluble in water and soluble in fats and organic solvents. They are white, odourless, and crystalline.

*Functions* — The D vitamins regulate the absorption, metabolism, and deposition of calcium and phosphorus in the body and hence control bone and teeth formation, among other functions. The metabolism of other minerals, such as magnesium and iron, as well as of carbohydrates, is also affected.

*Results of Deficiency* — Rickets is the most striking result, but apart from the effect on bones, the muscles become flabby and the whole body is affected. Also, susceptibility to various infections is increased.

*Hypervitaminosis* — Large excessive doses are harmful, particularly in the case of D<sub>2</sub>.

*Sources* — The provitamins are widely distributed, the commonest in higher animals and humans being 7-dehydro-cholesterol, and in plants and yeasts, ergosterol. The D vitamins do not occur in nature in appreciable quantities. Large amounts are found in fish livers; eggs, particularly yolks, and milk are good sources.

*Synthesis and Preparation* — The D provitamins have not been completely synthesized, but have been prepared chemically from sterols. Commercially, the chief preparation is of ergosterol from yeast; 7-dehydro-cholesterol is synthesized from cholesterol. The D vitamins are prepared from the provitamins by activation, ultra-violet light being the means most commonly employed. An intermediate compound is tachysterol, and to this is related dihydro-tachysterol (known as A.T.10), which has a certain amount of antirachitic activity, and increases the calcium content of blood serum.

*Assay* — Chemical and spectroscopic methods are not very accurate, and biological methods, employing rats or chicks, still hold the field. A recent physico-chemical method involving chromatographic absorption is promising.

*Standard* — 1 I.U.=0.025 $\gamma$  pure crystalline D<sub>2</sub> dissolved in 1 mg. olive oil.

*Requirements* — 400 to 800 I.U. daily for pregnant and nursing

women and for young children. For older children and adults the requirements will depend on the sunshine available and on individual utilization of calcium and phosphorus.

**Vitamin E** — *General Properties* — This is a group of three isomers,  $\alpha$ ,  $\beta$ , and  $\gamma$ -tocopherols, oils soluble in organic solvents and insoluble in water. They are readily oxidized and are destroyed by ultra-violet light. They are heat stable in the absence of oxygen and not attacked by acid. Anti-oxidants.

*Functions* — Function in plants doubtful, but probably concerned with cell growth. In animals and man, the vitamin seems to be associated with activities of the cell nucleus, and appears to be essential for normal reproductive function in both sexes.

*Results of Deficiency* — In animals, sterility in the male, interference with gestation in the female. Degeneration of muscles, also of nerve cells in the spinal cord. In bad cases, paralysis of the limbs. Encephalomalacia in chicks. Prolonged deficiency of the vitamin causes a secondary deficiency of vitamin A. Effects on humans is not known with much certainty, but appear to follow similar lines to those on animals.

*Hypervitaminosis* — Not known with this vitamin.

*Sources* — Chiefly in plants, particularly in wheat germ oil. The oils of other seed germs are also good sources and so are lettuce and watercress.

*Synthesis* — All the three E vitamins can be synthesized by reaction of hydroquinones with a phytyl compound, and the synthetic material, as the acetate, is that most commonly employed.

*Assay* — Biological assay, with comparison with synthetic racemic  $\alpha$ -tocopherol is superior to physical and chemical methods, which do not differentiate between the  $\alpha$ ,  $\beta$ , and  $\gamma$  isomers. Of the chemical methods, the best known is a colorimetric test, employing ferric chloride and dipyriddy, and an electrometric method using gold chloride.

*Standard* — 1 I.U.=1 mg. of synthetic racemic  $\alpha$ -tocopherol acetate in 0.1 g. of olive oil.

*Requirements* — Unknown for man.

**Vitamin K** — This comprises at least two members, known as  $\alpha$ - and  $\beta$ -phyloquinone, as well as 2-methyl-1,4-naphthoquinone.

*General Properties* —  $K_1$  and  $K_2$  are soluble in organic solvents but not in water; 2-methyl-1,4-naphthoquinone is slightly soluble in water. Heat stable, but sensitive to light and alkalis;  $K_1$  is an oil,  $K_2$  and 2-methyl-1,4-naphthoquinone are crystalline. All are yellow in colour.

*Functions* — The outstanding function of this group is to maintain the normal coagulation of blood, hence, its alternative names of prothrombin factor or anti-hæmorrhagic vitamin. It is involved in the formation of prothrombin, apparently in the liver. It is also antagonistic to dicumanol (3,3'-methylenebis (4-hydroxycoumarin)), which causes sweet clover disease in cattle.

*Results of Deficiency* — With the reduced amount of prothrombin in the blood, rate of clotting is prolonged. Actual hæmorrhage occurs,

particularly in new-born babies. It is said that more than 20 per cent. of the 128,000 infants who do not survive each year in the United States show evidence of cerebral hæmorrhage, attributable to vitamin K deficiency. Defective prothrombin formation is also noticed in various diseases such as obstructive jaundice, sprue, etc.

*Hypervitaminosis* — None.

*Sources* — Occurs in plants and bacteria. Richest sources are berries of the European mountain ash and green leaves of such plants as alfalfa, spinach, cabbage, and kale. Vitamin K is isolated chemically from these. The vitamin is formed in the cæcum and other parts of the alimentary tract of animals and man by the bacterial flora.

*Synthesis* —  $K_1$  can be synthesized in various ways, such as from 2-methyl-1,4-naphthoquinone and phytol, or from 2-methyl-1,4-naphthohydroquinone and phytol in the presence of catalysts;  $K_2$  has not been synthesized; 2-methyl-1,4-naphthoquinone can be synthesized by the oxidation of 2-methyl-naphthalene, by chromic acid in acetic acid.

*Assay* — Spectroscopically and by several colorimetric methods, but biological methods involving determination of clotting time of blood are superior.

*Standard* — None established.

*Requirements* — Apparently required by all animals, but amounts not known.

**Vitamin P** — *General Properties* — Beyond the fact that it is water soluble, properties not known, since it has not been obtained in the pure form.

*Functions* — Maintains condition of the blood capillaries. Suspected among other properties of being necessary for the absorption of vitamin C in the body.

*Results of Deficiency* — Hæmorrhagic conditions of the skin resulting from reduced resistance of the capillaries.

*Hypervitaminosis* — Not known.

*Sources* — Chiefly in citrus fruits, and more in the skin than in the juice. Also in the juice of paprika and probably of most plants.

*Assay* — A chemical method based on colour production with boric acid has been suggested, but biological methods, employing guinea pigs and rats, and based on hæmorrhages are at present the most satisfactory.

*Standard* — Not established.

*Requirements* — Not known.

**"VITREFLEX"** — Anticorrosive iron and steel building material made by application of a flexible and adherent enamel to a copper-containing iron or steel fired on at a high temperature; impervious to moisture and unaffected by temperature changes, marine, acid, and other corrosive atmospheres.

**"VITREOSIL"** — Trade-name for wares fashioned out of silica in a state of fusion by processes resembling those used with glass. (See Glass, and Silicon (Silica).)

**VITREOUS** — Glassy. (See Glass.)

**VITRIOL or OIL OF VITRIOL** — Strong sulphuric acid. (See also Blue Stone (Blue Vitriol), Green Vitriol, and White Vitriol.)

**VIVIANITE** — A mineral ferrous phosphate ( $3\text{FeO}, \text{P}_2\text{O}_5, 8\text{H}_2\text{O}$ ), of crystal system No. 5, and sp. gr. about 2.6.

**VOLATILE** — Light, ethereal; easily passing from liquid to gaseous state; used concerning a liquid or solid that has an appreciable vapour pressure at ordinary temperatures, but also where a substance is vaporized upon heating. *Sal volatile* (smelling salt) is ammonium carbonate.

**VOLTAMETER (Coulometer)** — Apparatus for measuring the amount or quantity of electric current passing through a circuit. Some types are based upon the electrolysis of liquids—water, for example, acidulated with a little sulphuric acid—and measuring the gases (oxygen and hydrogen) evolved. In other cases, the determination is made by ascertaining the quantity of metal deposited at the cathode from solutions exposed to the current—silver, and copper, for example, from their salt solutions. (See Electricity.)

**“VOLTOL” OILS** — Oils such as rape and marine animal oils, thickened by blowing, followed by electrical treatment (the high viscosity thus secured being due to oxidation and polymerization) and used amongst other applications for admixture with mineral oils as lubricants in the place of castor oil. Exposure of fatty oils to the electric glow discharge in hydrogen gas at low pressure yields polymerized products of high viscosity; thus, oleic acid gives about 16 per cent. of stearic acid.

The high viscosity of “Voltol” oils is attributed in part to the contained oxidation products and polymerization induced by the blowing, but chiefly to the production of dimolecular glycerides under the influence of the electric discharge, thus accounting for their high molecular weights, which are stated to be 1,200 and 1,000 for rape and whale “Voltol” respectively.

**“VOLTOLIZING” (“VOLTOLISIERUNG”)** — See “Voltol” Oils.

**VOLUME (Critical)** — The critical volume of a fluid is its specific volume in its critical state, or that occupied by 1 gram at the critical temperature. (See Critical Points, and Matter.)

**VOLUMETRIC ANALYSIS** — Methods for determining the amounts of chemical substances present in solutions by the employment of reagents of definite strength in connection with well-understood interactions. “Normal standard solutions” contain an equivalent weight (gram equivalent) of the substance dissolved in 1 litre (1,000 ml.), and decinormal solutions are of one-tenth that strength. Thus a normal solution of hydrochloric acid contains 36.47 grams per litre. To determine, for example, the amount of free iodine that may be contained in an acidified solution of potassium iodide, a standardized solution of sodium thiosulphate is employed—that is to say, a solution of predetermined strength—and this is gradually run into the subject mixture from a burette until the colour has entirely disappeared. It is then easy to calculate, from the known chemical interaction that takes place, the

amount of free iodine in the mixture. This interaction is represented as follows:  $I_2 + 2Na_2S_2O_3 = 2NaI + Na_2S_4O_6$ . The free iodine is converted into sodium iodide and the thiosulphate into tetrathionate, and knowing the amount of thiosulphate consumed, it is easy to calculate the amount of free iodine changed. If a little starch solution be added to the iodine solution just before the completion of the titration, a beautiful blue coloration is produced as long as free iodine is present. A means of stabilizing starch solution is by the use of salicylic acid.

For the determination of the amount of alkali or acid present in solutions, calculations are made based upon the amount of standardized solution of acid or alkali required respectively, by titration, to neutralize them; this point of neutrality (the end-point of the reaction) being ascertained by means of an indicator, or substance which undergoes a marked change of colour upon the change from alkalinity to acidity, or *vice versa*. The older indicators chiefly used were turmeric, cochineal, and litmus; then, later, methyl orange and phenolphthalein. See Indicators, Hydrogen-Ion Concentration, and pH Value for other indicators and their ranges.

Substances which change their colour as the H-ion concentration of their solutions change are used as indicators. Thus, phenolphthalein solutions, which are colourless when having  $[H^+] = 10^{-8}$ , become pink when the  $[H^+]$  is  $10^{-10}$  or less.

Methyl orange, lacmoid, and cochineal are insensitive to weak acids; litmus is typical of the indicators somewhat sensitive to weak acids; and phenolphthalein, turmeric, and rosolic acid are highly sensitive to weak acids. Methyl orange dissolved in water is turned yellow by alkalis and pink-red by acids.

Phenolphthalein dissolved in alcohol is colourless, but alkalis turn it deep pink, which is at once discharged by acids. Cresolphthalein has been recommended in place of phenolphthalein. Thymolsulphophthalein is a useful indicator in the liming of sulphonation mixtures, a red coloration indicating that free acid is still present; when the indicator shows a yellow colour, the end-point is near, and a blue colour shows that the mixture is alkaline. Dibromocresolsulphophthalein or dibromothymolsulphophthalein may be used as substitutes for litmus, the former changing from yellow to purple and the latter from yellow to blue in the passage from acidic to alkaline solution.

With respect to the hydrogen-ion method for using indicators in volumetric analyses, it must be understood that the H-ion normal solution contains one gram equivalent of *hydrogen-ion* per litre of solution, and this is employed as a basis for computing pH value (see same).

In titrations of acids and alkalis, the pH value of the solutions can be deduced from voltameter readings at all stages, and it may be used in preparing solutions of any desired pH value.

**Buffer action** may be described as the prevention of rapid changes in hydrogen-ion concentration of acid or alkaline solutions exercised by the presence of certain salts. Buffer solutions, presenting a range of

colours, can be made by the addition of suitable indicators to a series of solutions, using solutions of salts such as acetates, borates, and phosphates of the alkaline metals, to which the addition of acids or alkalis causes only small changes in the hydrogen-ion concentration, and they serve as standards of comparison with others of which the  $pH$  values have to be ascertained. (See Analytical Chemistry.)

*References:* *Volumetric Analysis*, by Francis Sutton (J. and A. Churchill, London); *Potentiometric Titrations*, by I. M. Kolthoff and N. H. Furman (Chapman and Hall, London); *The Colorimetric and Potentiometric Determinations of pH*, by I. M. Kolthoff (Chapman and Hall, London); *Indicators*, by I. M. Kolthoff and N. H. Furman (Chapman and Hall, London); *The Determination of Hydrogen-Ions*, by W. M. Clark (Williams and Wilkins, Baltimore); *Scott's Standard Methods of Chemical Analysis* (D. Van Nostrand Co., New York); article on "Analysis" in *Thorpe's Dictionary of Applied Chemistry*; Buffer Action, Hydrogen-Ion, Indicators,  $pH$  Value, and Reagents.

**VRIAC** — A French term for kelp. (See Barrilla, Iodine, Kelp, Sea-Weeds, and Varec.)

**VULCANITE** — See Rubber.

**VULCANIZATION** — See Rubber.

**WALNUT OIL**, expressed from the seeds of *Juglans regia* or *J. Sieboldiana*, a native of Persia and the Himalayas, and cultivated in Europe, is of pale yellowish-green colour and weak drying character, with sp. gr. 0.92 to 0.93; ref. ind. 1.4808 at 20° C.; sap. v. 192 to 197; i.v. 142 to 146; and solidifies at -27.5° C. The main constituent is linolic acid. It is soluble in alcohol and ether, and used in the varnish and paint trades and preparation of artists' colours. A recent description of a sample gives the acid value 92.3; in this instance the fruit yielded 26.54 per cent. kernel containing 4.99 per cent. water and 59.58 per cent. oil by pressing.

A sample of Californian walnut oil showed a content of 89.7 per cent. unsaturated and 5.3 saturated acids, the composition being given as oleic acid 17.6; linolic acid 72.8; linolenic acid 3.2; palmitic acid 4.6; stearic acid 0.9, with traces of myristic and arachidic acids, and 0.5 per cent. unsaponifiable matter.

Walnut extract is used in wood-staining and the paint and varnish trade, while the cake has some value as food for cattle and poultry.

**WARFARE (CHEMICAL)** — See Poisons.

**WASTES (TRADE)** — Many branches of industry related to chemistry produce wastes that are troublesome to deal with, not only to themselves but to the surrounding communities. As industrial sections become more and more congested this matter becomes a serious problem. Considerable attention is being given the subject in the United States by state and federal authorities. It cannot

be considered an ordinary sewage problem in many cases—it is a real chemical one that is frequently baffling to all concerned.

The wastes may be salts, acids, alkalis, or a wide range of organic materials such as those from packing houses, tanneries, fruit and vegetable canneries, breweries and distilleries, wood pulp and paper mills, beet-sugar factories, textile mills, and the dairy industries. Sometimes it may be possible to combine those from two or more different sources to partially solve the problem, as was done by one chemical plant in New Jersey, an account of which is given by V. L. King *et al.* in *Chemical Industries* (New York), 1941, p. 286, entitled "Calco Solves Raritan River Problem."

Treatment will depend first upon the physical condition of the waste, and second upon its concentration. The standard methods of filtration, sedimentation, evaporation, and drying would naturally be surveyed. If these do not provide a satisfactory answer, attention would be directed to neutralization, precipitation, air oxidation, biological action, chlorination, or even treatment with activated carbon.

The concentrations in parts per million of certain chemicals—a very abbreviated list—stated to be critical to fish life are as follows: copper sulphate 0.14 for trout, to 2.00 for black bass; naphthalene 5; cyanide 10; ammonium hydroxide 10; phenols 10; thiocyanate 200; pyridine 400; and ammonium sulphate 500.

For neutralization of acid wastes the cheapest material would doubtless be limestone ( $\text{CaCO}_3$ ) or lime ( $\text{CaO}$ ). If the acid produces an insoluble calcium compound such as the sulphate, then the limestone must be ground very fine, say 200-mesh, and be agitated.  $\text{Al}_2(\text{SO}_4)_3$ , as plain sulphate or as alum, or a ferric salt serves as an excellent coagulating agent. Chlorine added at the proper stage will destroy bacteria, and as in the case of city drinking water unpleasant odours are removable by the use of activated carbon. This last treatment is effective in removing the odour and taste of phenols plain or chlorinated.

An interesting study has been made by W. W. Hodge on "Wastes Problems of the Iron and Steel Industries" (*Ind. Eng. Chem.*, **31**, 1364 (1939)). Two methods of treating iron pickle liquor are suggested that are of chemical interest: (1) Addition of ammonia to precipitate ferrous hydroxide followed by air oxidation to the ferroferric oxide black precipitate stage, which material can be easily settled and decanted. This leaves ammonium sulphate recoverable in the solution. (2) Addition of very fine limestone with aeration, because ferrous is not completely precipitated and ferric is. This plan was varied by adding some slaked lime ( $\text{Ca}(\text{OH})_2$ ) with the limestone. A third study made by Hodge was the treatment of low-grade manganese ore with the pickle liquor and separating the gangue by filtration. From the solution he was able to obtain a product containing 60 per cent. manganese.

Studies made of corn products wastes showed that when these are mixed with an equal volume of domestic sewage, the whole can be satisfactorily treated by the activated sludge process or on trickling filters. Similar studies on phenol wastes successfully used (1) volatili-

zation with steam, and passing the vapour into sodium hydroxide from which phenols were recovered by acidification; and (2) solvent extraction by oil, and the recovery of phenol from the oil layer by similar sodium hydroxide treatment as just described.

Where the wastes are organic and in quantity they may be evaporated and dried and burned as fuel, thus yielding more or less economic return.

*References* : Symposium on Industrial Wastes, in *Ind. Eng. Chem.*, **39**, 560–676 (1947); "Bibliography on Chemical Wastes," by R. W. Hess (*Ind. Eng. Chem.*, **39**, 676 (1947)); "Utilization of Agricultural Wastes," by M. Levine *et al.* (*Ind. Eng. Chem.*, **27**, 195 (1935)); "Treatment of Trade Waste with Activated Carbon," by F. D. Snell (*Ind. Eng. Chem.*, **27**, 825 (1935)); P. J. Wilson, in *Proceedings of the American Gas Association*, 1929, 934 (phenols); Milwaukee (Wisconsin) Sewerage Commission *Seventh Annual Report* (1920) (phenols); National Cannery Association *Research Bulletin* **28-L** (Dec. 1939); *Waste in Industry*, by the Committee on Elimination of Waste in Industry of the Federated American Engineering Societies (McGraw-Hill Book Co., New York); *Liquid Fuel from Agricultural Residues*, R.I. 4653 (1950) (U.S. Bureau of Mines, Pittsburgh, Pennsylvania); and Sulphur (Recovery).

**WATER (Hydrogen Monoxide) ( $H_2O$ )** — Water is the most familiar chemical substance. As inhabitants of the earth we encounter water principally as a liquid, of greater or less purity, but it is also present in the gaseous atmosphere that surrounds us, and seasonally and locally as ice. Water is the same chemical substance that, in one case, as a constituent of the atmosphere, is available, upon cooling, as in a summer evening, to support the growth of plant life, and, in another case, as a substance in the cracks of rocks, does, upon freezing, expand and thus rend these same rocks to pieces that ultimately furnish soil for plant growth.

Plant life and animal life are alike dependent upon a supply of water. Foods as eaten are frequently 90 per cent. water, and the body fluids, except milk, are about 99 per cent. water. So commonplace is our lack of recognition of the importance of water that is an ordinary occurrence for us to stress, say in the matter of foods, everything but water.

Snowy glaciers and polar ice fields are, along with rain water, the only practical sources in nature of water that approximates to purity. It is the small proportions of other materials, therefore, in the water we encounter that, on the one hand, sustain life, and, on the other hand, menace our existence.

All of the water that flows over the earth or is maintained in reservoirs—from the town water-supply to river, lake, and ocean water—contains inorganic and organic dissolved and suspended matter.

**Sea-water** contains salts washed out of the earth's surface, including large quantities of common salt and magnesium chloride, and has a specific gravity of about 1.025 to 1.027, as compared with ordinary water, 1.000. The water of the English Channel contains 28.05 parts



NaCl, 3.66 parts of  $MgCl_2$ , and 4.7 parts of other mineral substances in each 1,000 parts. Potassium salts are present to the extent of about  $\frac{1}{10}$  to  $\frac{1}{5}$  of sodium salts, and the ratio of bromine to chlorine is about 1 to 288. See Sodium (Chloride). The *Challenger* expedition determined the temperature of water at the bottom of the ocean to be  $+0.3^\circ C$ . at a depth of 2,800 fathoms (5,100 m.). This and succeeding expeditions have surveyed the waters of the globe, as to temperature and salt contents. In fact, oceanography has become a recognized branch of science. For the analyses of many sea and river waters, for the turbidity of river waters, the denudation of the land surface of the earth, the hardness of publicly supplied waters and their sanitary analyses, as well as the seasonal evaporation of water at various places, see the article on Water in *Van Nostrand's Scientific Encyclopedia* (D. Van Nostrand Co., New York; Chapman and Hall, London); also *Recent Advances in the Chemistry and Biology of Sea Water*, by H. W. Harvey (Cambridge Univ. Press).

**Rain-water**, as collected in country places where the air is not fouled with smoke and other emanations, is as nearly pure as it is ordinarily found in nature, but even then it contains about  $2\frac{1}{2}$  volumes of air dissolved in each 100 volumes by measure. It is a sort of distilled water; the heat of the sun evaporates water from the earth and the sea, and then, when the air is more or less saturated with the water vapour and becomes cold enough, it is transformed and falls as rain, snow, or hail. Soft water is water which is more or less devoid of substances held in solution, so that freshly collected rain-water is quite soft in character.

Many gases are more or less soluble in water, including nitrogen, oxygen, carbon dioxide, and argon, the degree varying with the temperature and pressure. (See Solubilities.)

Natural mineral and **spring waters** are of many diverse characters, embracing some (like Vichy spring) of alkaline character containing sodium bicarbonate; another variety of much the same class, but containing much sodium chloride in addition (such as Ems, Droitwich, etc.); alkaline salt waters containing sodium sulphate and bicarbonate (such as Carlsbad and Marienbad); various types of chalybeate waters containing iron in differing forms (such as Harrogate, Hamburg, and Saratoga); sulphuretted waters containing hydrogen sulphide (such as Harrogate, Aix, and Baden); earthy alkaline waters such as found at Bath and Pisa; thermal waters containing saline ingredients, like those occurring at Clifton and Buxton, etc.; all dependent upon geological conditions and the chemical character of their environment.

Water, as ordinarily supplied for drinking purposes, containing impurities in the form of substances dissolved out of the earth with which it comes naturally into contact, furnishes supplies roughly classified as "hard" or "soft" in character. The so-called "temporary hardness" is mainly derived from the presence of calcium carbonate or chalk in solution, which is deposited as a fur or cake in tea-kettles and boilers. This deposition is due to the expulsion of carbon dioxide previously contained in the water, and which by its

presence, and until expelled by the heat, holds the chalk in solution. Such waters may be softened therefore to some extent by boiling, as already explained, or by the addition of lime, which, by entering into combination with the carbon dioxide, forms insoluble calcium carbonate ( $\text{CaO} + \text{CO}_2 = \text{CaCO}_3$ ), and this is deposited along with the carbonate previously held in solution by the carbon dioxide thus removed. The "permanent hardness" of natural waters is largely due to the presence of the sulphates of calcium and magnesium, the degree of hardness being dependent upon the nature of the geological formation in which the water is found, and in some cases barium carbonate may be usefully employed for removing the sulphates. (See Water Conditioning.)

## ANALYSES OF SOME NATURAL WATERS AND BRINES

Values given in weight per cent.

	Cheltenham, England	Vichy, France	Wiesbaden, Germany	Carlsbad, Bohemia	Salsomaggiore, Italy	Syracuse, New York Brine	Cleopatra Spring, Yellowstone National Park	Norris Basin, Yellowstone National Park
Cl	38.01	6.17	56.58	11.52	61.09	58.85	10.09	36.61
SO <sub>4</sub>	20.89	3.75	0.78	31.19	0.18	2.29	30.34	1.84
CO <sub>3</sub>	4.22	45.57	3.13	19.15	—	0.01	21.65	0.15
Na	32.80	35.27	32.60	32.49	34.04	37.29	7.50	21.44
K	0.72	2.88	1.16	1.35	—	0.03	2.95	4.45
Ca	1.85	2.29	4.05	2.23	3.21	1.28	17.76	0.39
Mg	1.37	1.11	0.61	0.65	0.82	0.23	4.21	0.08
SiO <sub>2</sub>	0.14	1.32	0.76	1.34	0.01	—	2.98	31.72
Al <sub>2</sub> O <sub>3</sub>	—	—	—	—	—	—	0.54	0.76
		Other 1.64	Other 0.33	Other 0.13	Other 0.65	Br 0.01	Other 1.98*	Other 2.56*

\* Principally borate.

**Sand filtration** of water for domestic and industrial use is greatly employed, and combines several distinct processes. The sand itself presents a barrier to all suspended particles of greater size than its interstices, and thus forms a layer of still finer pockets in which bacteria are arrested, thus producing a slimy gelatinous film which plays an important part in the purification of the water. Storage, absence of adequate nutrient material, and dissolved oxygen are destructive agencies against *B. Coli* and some other bacteria. The addition of alum or aluminium sulphate to produce a gelatinous floc before filtration is standard practice.

Chloride of lime and chlorine are effective agents for the **sterilization** of water to be used for drinking supplies. The addition of 15 pounds chloride of lime to 1,000,000 gallons of Thames water destroys the microbes from previous sewage contamination more effectually than by passage of the water through a reservoir containing 80 days' supply,

while 1 to 2 parts of chlorine have been found sufficient to sterilize some 5,000,000 parts of water in an hour or so. The odour and taste which are sometimes developed upon the treatment by chlorine are effectively removed by activated carbon.

The "Catadyn" process of water sterilization depends upon the germicidal action of silver deposited upon porcelain or sand in a finely divided state so as to present a large reaction surface. It is stated to reduce the bacterial content by 90 per cent. in two hours, and, after removal from the apparatus and standing two more hours, complete sterilization is said to be attained.

#### ABSOLUTE DENSITY OF WATER AT VARIOUS TEMPERATURES

TEMPERATURE ° C.	DENSITY Grams per Cubic Centimetre	TEMPERATURE ° C.	DENSITY Grams per Cubic Centimetre
0	0.999841	16	0.998943
4	0.999973	20	0.998203
5	0.999965	25	0.997044
10	0.999700	30	0.995646
15	0.999099		
Specific gravity 15° C./4° C. 0.99913			
Specific gravity 20° C./4° C. 0.99824			
Specific gravity 25° C./4° C. 0.99708			
Specific gravity 15.56° C./15.56° C. multiplied by 0.99908 equals specific gravity			
15.56° C./4° C.			
(15.56° C. equals 60° F.)			

#### WATER VAPOUR PRESSURE AT VARIOUS TEMPERATURES

TEMPERATURE ° C.	WATER VAPOUR PRESSURE Mm. of Mercury	TEMPERATURE ° C.	WATER VAPOUR PRESSURE Mm. of Mercury
-10 (ice)	2.0	80	355
0	4.6	81	380
10	9.2	90	526
20	17.5	97	682
30	31.8	98	707
40	55.3	99	733
50	92.5	100	760
60	149	102	816
70	234	120	1520

Water boils at 100° C. (212° F.), freezes at 0° C. (32° F.) (see Crystals) to a crystalline solid having a specific gravity of 0.92, attains its maximum density at 4° C., and, although slightly compressible, is commonly regarded as incompressible. At 20° C., a pressure of 1,000 atmospheres causes a contraction of volume of 4 per cent. Its vapour is decomposable at a very high temperature (at and above 1,000° C.), and readily so in the presence of oxidizable substances such as iron and coke. Its importance as a catalyst in chemical reactions is referred to under the heading of Chemical Interactions and is emphasized by Baker's work on the absence of reaction between dry substances (see Heat). See also J. W. Smith's book entitled *The Effects of Moisture on Chemical and Physical Changes* (Longmans, Green and Co., London).

Water vapour in the air plays an important role in our own comfort, the presence of relatively large amounts of water vapour at high

temperatures being responsible for the discomfort accompanying muggy days. One of the advantages of true air conditioning is that it lowers the humidity. Humidity is defined as the number of pounds of water vapour contained in one pound of dry air. This *absolute humidity* value for air *saturated* with water vapour is :

TEMPERATURE		HUMIDITY
° C.	° F.	Pounds of Water Vapour per pound of Dry Air
15	59	0.0107
20	68	0.0147
25	77	0.0201
30	86	0.0272
35	95	0.0366

*Relative humidity* is the percentage of contained water vapour referred to the saturation value at the given temperature.

When water is boiled it takes the gaseous form of steam, and when this is conducted away and cooled it becomes condensed as water once more. Purified from any mineral constituents by distillation or ion-exchange, water is employed in laboratories for making chemical reagents and other purposes. Ice made from distilled water, as well as the first frozen sides of ordinary ice, can frequently be used to advantage as a source of pure water.

Steam is an effective germ destroyer, and there are a number of so-called disinfectors or destroyers by which it is generated and used for the sterilization of clothing and bedding.

Water has greater solvent power than any other liquid in respect of range of substances, and therein lies one of its most interesting scientific and industrial aspects. (See Solubilities, and Solution and Solvent Action.) It also enters largely into the constitution of many chemical substances, such as hydroxides, hydrates, and salts, being combined in the last-named substances as so-called water of crystallization. Copper sulphate, for example, crystallizes in a form containing 5 molecules of water ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) and magnesium sulphate with 7 molecules ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ). Sodium carbonate is known in chemical association with water in several forms, including  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ , and  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ . In all such cases it must be borne in mind that the water molecules form integral parts of the compounds.

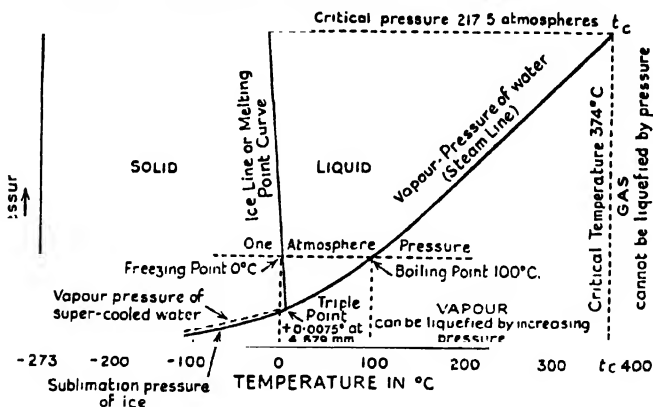
In many cases, the colours of salts are dependent upon the amount of water of crystallization, as instanced by cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), which is pink, but when gently heated to  $120^\circ \text{C}$ . becomes blue in colour by the loss of its water. Another compound, namely, magnesium platinocyanide, in its crystalline form contains 7 molecules of water  $\text{MgPt}(\text{CN})_4 \cdot 7\text{H}_2\text{O}$  and is of a bright scarlet colour, but when heated to  $50^\circ \text{C}$ . it loses 2 molecules of water and becomes  $\text{MgPt}(\text{CN})_4 \cdot 5\text{H}_2\text{O}$ , which is of a canary-yellow colour, and upon raising the temperature to  $100^\circ \text{C}$ . a white salt finally results, having the composition  $\text{MgPt}(\text{CN})_4 \cdot 2\text{H}_2\text{O}$ . (See also Efflorescence, and Deliquescence.)

Some particulars respecting the formation of water will be found

under the headings of Catalysis, and Hydrogen. The heat of formation of liquid water at 25° C., and a constant pressure of 1 atmosphere as determined by F. D. Rossini, is  $285,890 \pm 40$  absolute joules.

Water seems to contain no definite polymers, in spite of assumptions to that effect that have frequently been made. It consists, according to Hildebrand, of continuous polar lattices, muddled up by thermal agitation. Liquid water has a high dielectric constant, namely 81, that points to a highly polar molecule, and to its action as a strongly ionizing solvent. The water molecule is unsymmetrical, the angle between the bonds of oxygen leading to the two hydrogen atoms being 104.5 degrees. The distance between centres of the oxygen atom and each hydrogen atom is 0.96 Angstrom units. In ice the oxygen atoms are regularly arranged (see Bernal and Fowler, *J. Chem. Phys.*, 1, 515 (1933), and Katzoff, *J. Chem. Phys.*, 2, 841 (1934)). An ice-tridymite structure predominates near 0° C., a quartz-like structure at ordinary temperatures, and an ammonia-like structure above 200° C.

#### WATER. TEMPERATURE-PRESSURE RELATIONSHIP



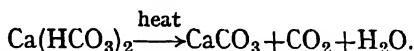
Each oxygen atom is linked to two others by hydrogen bonds, according to the X-ray studies of Warren in *Physical Review*, 44, 969 (1933).

**References:** "Industrial Water Supplies," their requirements, development, and design, by S. T. Powell and H. E. Bacon (*Ind. Eng. Chem.*, 29, 615 (1937)); *The Technology of Water*, by A. A. Pollitt (E. Benn, London); *Examination of Water*, by W. P. Mason and A. M. Buswell (John Wiley and Sons, New York); *Elements of Water Bacteriology*, by Prescott and Winslow (Chapman and Hall, London); *Elimination of Taste and Odour in Water*, by J. R. Bayliss (McGraw-Hill Book Co., New York); *Water Purification*, by J. W. Ellms (McGraw-Hill Book Co., New York); *Water Purification Plants and Their Operation*, by M. F. Stein (John Wiley and Sons, New York); *Water-Treatment and Purification*, by W. J. Ryan; *The Examination of Waters and Water Supplies*, by Thresh and Suckling; Brine, Filters, Soap, Steam, Water Conditioning, and Water Gas.

**WATER (Heavy)** — See Hydrogen (Heavy).

**WATER CONDITIONING** — Before using natural waters of any kind they must be adapted to the particular use for which the water is designed. Water-conditioning processes consist of two types, namely, softening and purification.

**Softening** is the term applied to those processes which remove or reduce the hardness of water. Hardness in water is due to objectionable amounts of dissolved salts of calcium and magnesium which form insoluble soaps and clog boiler feed lines. Temporary hardness in water is due to the presence of bicarbonate ( $\text{Ca}(\text{HCO}_3)_2$ ), which is destroyed upon heating by forming insoluble carbonate ( $\text{CaCO}_3$ ), carbon dioxide ( $\text{CO}_2$ ), and water ( $\text{H}_2\text{O}$ ). The following equation illustrates this reaction :



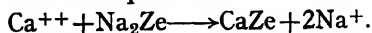
Permanent hardness is due to the presence of chlorides and sulphates of calcium and magnesium. Permanent hardness is not removed by heating. Hardness is generally expressed as parts per million (p.p.m.) or grains per gallon in terms of dissolved calcium and magnesium salts *equivalent to calcium carbonate*. (One grain per gallon is equivalent to 17.1 p.p.m.)

In addition to dissolved calcium and magnesium salts, which cause hardness, water also has dissolved in it sodium salts, silica, alumina, iron and manganese salts, and air in varying amounts depending upon the past history of the water. Boiler feed water should not corrode boiler plates and tubes, nor form scale on the plates or in the tubes to cause unequal heating and expansion, heat loss, and clogging of the tubes.

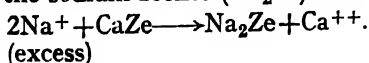
**Purification** of water usually refers to the removal of organic matter and harmful micro-organisms so that the water is potable and safe for domestic use. In purification, hardness is not usually a factor, except in laundering.

The following processes are utilized either separately or in conjunction with each other in conditioning water for various industrial and domestic purposes.

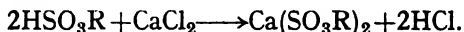
**I. Zeolite Softening Process** (Cation-exchange system).—Zeolite (Ze) is the name applied to a group of hydrated aluminosilicates that easily exchange certain cations like  $\text{Na}^+$  and  $\text{K}^+$  for  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ . When hard water is passed over sodium zeolite ( $\text{Na}_2\text{Ze}$ ) the  $\text{Ca}^{++}$  ions and  $\text{Mg}^{++}$  ions are removed from solution by exchange for the sodium ions according to the ionic equation :



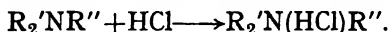
When nearly all the sodium ions in the zeolite have been replaced by  $\text{Ca}^{++}$  ions and  $\text{Mg}^{++}$  ions the zeolite is treated with a brine containing excess  $\text{NaCl}$  whereupon the  $\text{Na}^+$  ions replace the  $\text{Ca}^{++}$  ions and  $\text{Mg}^{++}$  ions to re-form the sodium zeolite ( $\text{Na}_2\text{Ze}$ ) thus :



**II. Demineralization or the Deionizing process.**—Certain synthetic ion-exchange materials (resins) remove completely the dissolved salts from ordinary water. These materials belong to two classes, namely, cation exchangers and anion exchangers. In the cation exchanger the metallic cation of the dissolved salt is replaced by  $H^+$  ion, thus producing an acidic condition in the water. This reaction can be expressed thus: the cation-exchanger ( $HSO_3R$ ) reacts with dissolved salt ( $CaCl_2$ ) to produce the salt of the cation-exchanger  $Ca(SO_3R)_2$  and free acid ( $HCl$ ):



The anion exchanger takes the water coming from the cation exchanger and removes the acid, thus leaving pure, demineralized water as follows. The anion exchanger ( $R_2'NR''$ ) reacts with the acid to form a stable salt ( $R_2'N(HCl)R''$ ) according to the reaction:

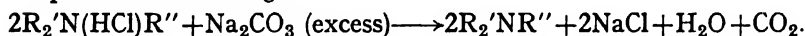


After use the cation exchanger and the anion exchanger are regenerated to their initial condition by treating with sulphuric acid and sodium carbonate solutions, respectively, according to the following equations:

Spent cation exchanger:

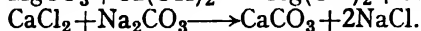
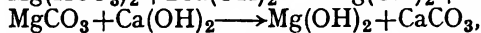
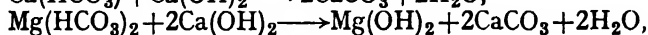
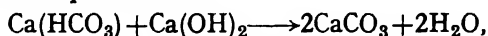


Spent anion exchanger:



This method is competitive with distillation for making pure water.

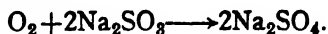
**III. Lime-soda Process.**—By adding calculated measured quantities of  $Na_2CO_3$  and  $Ca(OH)_2$  the magnesium and calcium ions can be removed by precipitation as insoluble  $CaCO_3$  and insoluble  $Mg(OH)_2$ . Typical equations are:



**IV. Phosphate Conditioning.**—Sodium hexametaphosphate  $((NaPO_3)_6)$  softens water by removing  $Ca^{++}$  ions,  $Mg^{++}$  ions,  $Fe^{+++}$  ions,  $Al^{+++}$  ions as soluble phosphate complexes, and thus prevents the formation of scale or insoluble soap. This compound also disperses previously formed scale and insoluble soap.

**V. Silica removal** is sometimes necessary in feed water for high-pressure boilers. This is accomplished by adsorption on magnesium hydroxide.

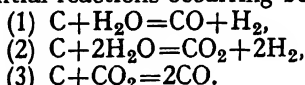
**VI. Deaeration** is sometimes necessary to stop corrosion problems in special processes; this is accomplished by allowing water to cascade downwards over a series of trays to meet a current of uprising steam. Dissolved oxygen can also be removed chemically by sodium sulphite according to the equation:



**VII. Water Purification** is accomplished when organic material and harmful micro-organisms are removed. This is done by coagulation with aluminium sulphate or ferric sulphate, followed by filtration through sand. A further filtration through activated carbon serves to remove objectionable odours. Chlorine is added in controlled amounts to destroy micro-organisms.

*References:* *Examination of Water*, by Mason and Buswell (John Wiley and Sons, New York); *Roger's Manual of Industrial Chemistry*, by Furnas (D. Van Nostrand Co., New York); *Boiler Chemistry Feed-Water*, by J. H. Paul (Longmans, Green and Co., London); "Ion Exchange between Solids and Solutions," by Walter (*J. Franklin Inst.*, **232**, 305 (1941)); "Demineralizing Solutions by a Two-step Ion Exchange Process," by Tiger and Sussman (*Ind. Eng. Chem.*, **35**, 186 (1943)); "Ion Exchange Resins," by Meyers (*Ind. Eng. Chem.*, **35**, 859 (1943)); "Prevention of Calcium Deposits in Process Water," by sodium metaphosphate and by sodium pyrophosphate, by B. H. Gilmore (*Ind. Eng. Chem.*, **29**, 584 (1937)).

**WATER GAS** is obtained by alternately passing air and steam over red-hot coke or powdered coal, which has the effect of decomposing the water vapour and producing a mixture of hydrogen and carbon monoxide gases, the essential reactions occurring being represented as:



The exothermic reaction which takes place during the passage of air yields carbon dioxide and some carbon monoxide, and the subsequent endothermic reaction from the passage of steam yields a mixture of carbon monoxide and hydrogen. A modified process employs steam and coke only. Incidentally, a variety of tar is produced in the process, from which benzol, phenol, etc., can be obtained by fractional distillation.

At 1,000° C. water gas is stated to contain about 49.5 per cent. carbon monoxide and 50 per cent. hydrogen, together with small quantities of carbon dioxide and water vapour. To make this mixture of gases (which otherwise burns without light) luminous when burning, it is, when this is desired, mixed with oil vapours, and employed for mixing with ordinary coal gas. The analysis of a water gas published by J. Hall is as follows: 46.8 per cent. hydrogen, 1.4 per cent. methane, 41.4 per cent. carbon monoxide, 0.1 per cent. oxygen, 3.1 per cent. carbon dioxide and hydrogen sulphide, and 7.2 per cent. nitrogen, having a calorific value of 296 B.Th.U. per cubic foot.

Water gas specially prepared can be utilized for the production not only of hydrogen, but also of methane, methyl alcohol, and "Synthol," and in the Fischer-Tropsch and Oxo reactions.

**WATER GLASS** — See Sodium (Silicate).

**WATERPROOFING** — "The basic principle in the application of a water-proofing chemical is that its presence in or on a fibrous substance modifies the surface tension between the water and the substance of the

fibre." Rubber dissolved in various solvents is used for the production of waterproof sheetings, the fabrics so coated being subsequently "cold cured" by passing them through a solution of sulphur chloride in carbon disulphide. Various synthetic resins have proved useful in waterproofing. Fabrics treated in this way are stated to have shown remarkable water-resisting quality, and proof against mildew.

**WATER SOFTENING** — See Water Conditioning.

**WATT** — The unit of power in the C.G.S. system, or the capacity to deliver 1 joule in 1 second. One kilowatt equals 1,000 joules per second or 1.341 horse-power; 760 kilowatts equals 1,000 horse-power; 1 kilowatt equals 238.7 calories per second.

**WATTLE** — Bark from the Australian wattles, *Acacia pycnantha*, *A. mollissima*, and *A. binervata*, containing from 25 to 45 per cent. tannin, used in tanning, and of some promise as a paper-making material. Most of the supplies come from Australia and Natal, and experiments have shown that the plants can be readily grown in Ceylon. It is reported that 33,000 acres are under cultivation in East Africa. (See Tannins.)

**WAVE LENGTHS** — The unit of wave length is the Ångström, being the ten millionth of a millimetre ( $10^{-7}$  mm.). Waves of light from the sun or a lamp range in length from the 40,000th of an inch to half that amount. Hertzian (wireless) rays range up to some thousands of metres in length; heat, light, and ultraviolet rays vary from 0.4 mm. to  $1.2 \times 10^{-6}$  mm. X-rays range from 12 to about 0.5 millimicrons; gamma rays about 0.01 millimicron. The accompanying chart makes clear some of the most important relationships and dimensions of the ether spectrum. The waves all travel at the same velocity as light, namely, 186,300 miles per second.

See Twyman and Smith on *Wave-length Tables for Spectrum Analysis* (Adam Hilger and Co., London); Energy, Radiation, Radioactivity, Ultra-Violet Rays, and X-Rays.

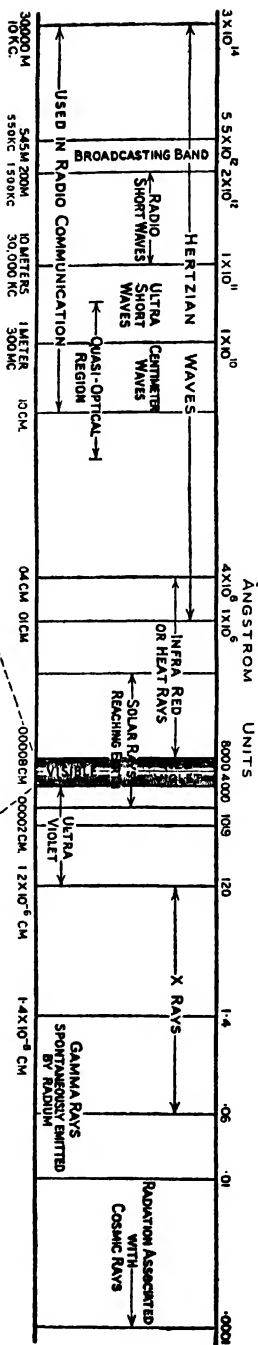
**WAVELLITE** — A natural aluminium phosphate ( $2\text{Al}_2(\text{PO}_4)_3 \cdot \text{Al}_2(\text{OH})_6 \cdot 9\text{H}_2\text{O}$ ) of crystal system No. 4, and sp. gr. 2.3.

**WAXES** — Are esters of monohydric alcohols and fatty acids of high molecular weight, together with some free acids and free alcohols. The "waxes" of mineral origin consist mainly of paraffin hydrocarbons, such as paraffin wax, and strictly speaking are not waxes at all. A typical wax is beeswax, which occurs as a yellowish-brown solid with a granular fracture. It is brittle when cold, but becomes plastic when warmed, and may be bleached to "white wax" by means of moist air with or without sulphur dioxide. It contains about 80 per cent. of myricin (myricyl, or mellisyl palmitate) and about 20 per cent. of cerotic acid. Yellow beeswax, *British Pharmacopœia*, must fulfil the following specifications: acid value 17–23; ester value (saponification value) 70–80; ratio number 3.3–4.2. It must also comply with limit tests for Fats, Fatty Acids, Japan Wax, and Resin; also for Ceresin and other waxes, including paraffin waxes.

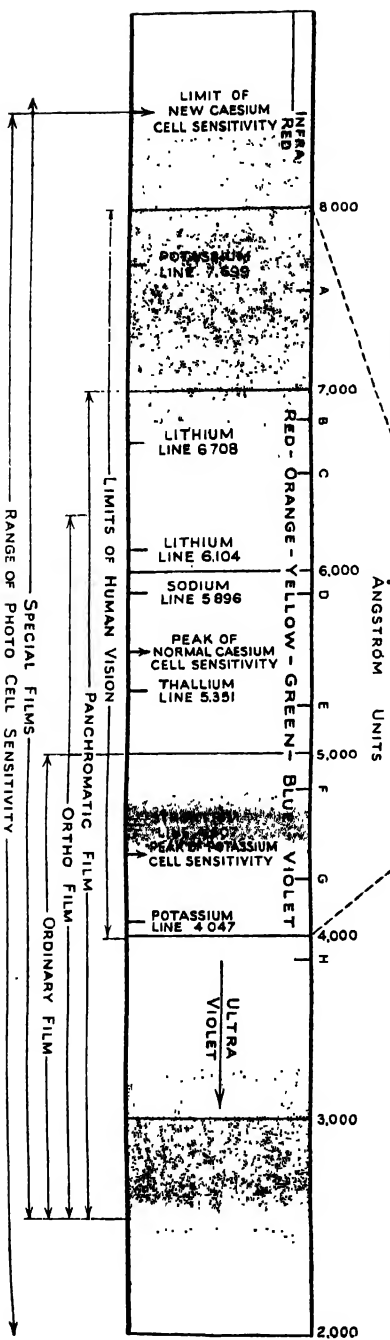
# WAVE LENGTHS

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## THE ETHER SPECTRUM



## THE PHOTO-ELECTRIC SPECTRUM



**Bayberry Wax** (Myrtle or Myrica, Candleberry, Bayberry, Laurel Wax, Wax-berry Wax), from the bark of the *Myrica cerifera* (a native of the United States) and other species, is green in colour, and consists of palmitin, palmitic acid, myristin, and lauric acid. It melts at 40° to 44° C.; sap. v. 208·7, sp. gr. 0·97 to 0·99, ref. ind. 1·4363 at 80° C., and is used in candle-making. Certain species of *myrica* are found at the Cape of Good Hope. The bark is used in medicine.

**Candelilla Wax** is found as an excretion on *Euphorbia antisyphilitica* (growing in North Mexico and southern parts of the United States), from the leaves and stalks of which it is obtained by boiling in water and adding some sulphuric acid, the yield being about from 2 to 3 per cent. It is soluble in benzene, turpentine, and carbon tetrachloride, and used in making polishes, candles, varnishes, sealing wax, gramophone records, etc. It is yellowish-brown, opaque to translucent, and said to contain a hydrocarbon ( $C_{30}H_{62}$ ) of m.p. 60° C. among other constituents; m.p. about 64° to 67° C., sp. gr. 0·983 to 1·00, sap. v. 46 to 65, i.v. 37, acid v. about 20, and ref. ind. 1·4555 at 71° C.

**Carnauba Wax** is obtained as a yellowish-white or green, sticky exudation from the leaves and the berries and stalks of a palm (*Copernicia cerifera*) growing in Brazil and the southern parts of America, which are coated with it, and said to consist largely of myricyl cerotate and myricyl alcohol ( $C_{29}H_{59}CH_2OH$ ), in which respect it resembles beeswax, for which it is used for some purposes as a substitute, also for making candles, varnishes, shoe and other polishes, phonograph records, etc. Its sp. gr. ranges from 0·990 to 1·000 at 15° C., m.p. 83° to 91° C., i.v. 13, sap. v. 78 to 88; it is soluble in hot alcohol and ether. After sun-drying it is refined by melting and bleaching with either fuller's earth, chromic acid, hydrogen peroxide, or potassium dichromate, and is marketed in a number of varieties, named "Arenosa" (sandy), "Gordurosa" (fatty), "Mediana" (medium), "Primeria" (first), and "Flor" (flower), in order of quality. It is also said to contain a large proportion of hydrocarbons, one sample giving 54·3 per cent. content.

**Ceresine** is a white wax-like substance obtained by purification of ozokerite with strong sulphuric acid, followed by filtration in a melted condition through animal charcoal. It is used for sizing, in candle-making, and for admixture with beeswax; sp. gr. 0·92 to 0·94, m.p. 74° to 80° C.; soluble in alcohol, benzol, etc.

**Chinese Wax** (Cerotin, Pela), or vegetable insect wax, is formed on the branches of a species of ash-tree (*Fraxinus chinensis*) from the secretion of the coccus insect (*Coccus ceriferus*). It resembles spermaceti; consists for the most part of a ceryl cerotate; is used in China for candle-making, and here for making leather polishes, and in sizing paper, etc. It admits, to some extent, of saponification with potash; is white to yellowish in colour, of sp. gr. 0·970, sap. v. 80 to 93, i.v. 1·4, m.p. 80° to 83° C., and is soluble in alcohol, benzol, and chloroform.

**Coca Wax** ( $C_{33}H_{66}O_2$ ) is obtained from the leaves of plants of the genus *Erythroxycæ*, including the *Erythroxylon coca* plant cultivated

in Java, Ceylon, Peru, Bolivia, and Brazil, and used for chewing. After purification, it is a white amorphous substance which melts at 70° C. and is readily soluble in hot alcohol. (See Cocaine.)

**Coccerin Wax** — The wax of the cochineal insect.

**Cotton-Seed Wax** — Contained in raw cotton to the extent of from 0.5 to 1 per cent. (See Cotton.)

**Cow-Tree Wax** is obtained by evaporating the latex of the cow-tree (*Palo de vaca*, *Brosimum galactodendron*, of the Cordilleras and Caracas), which is used as milk. It resembles beeswax in some general characters and admits of saponification.

**Emulsifying Wax** — A yellowish, wax-like substance, containing 10 per cent. of sodium lauryl sulphate and 90 per cent. of cetostearyl alcohol. It is self-emulsifying on admixture with water and is used in pharmacy for the preparation of emulsified ointment bases and for the formulation of cosmetic creams. A number of proprietary preparations are of the same or similar composition. "Lanette Wax S.X." consists of a mixture of cetyl and stearyl alcohols of which 10 per cent. have been sulphated. "Tenapol" is issued in two grades, "Tenapol I" containing sodium oleyl sulphate and "Tenapol II" containing sodium lauryl sulphate. "Empiwx" is issued in several grades, one of which consists of sodium lauryl sulphate and cetostearyl alcohol. "Polawax" is an emulsifying wax containing a non-ionic wetting agent in admixture with cetostearyl alcohol.

**Flax Wax** is dark green or brown, hard, and takes a high polish. Its composition ranges in sp. gr. from 0.963 to 0.985, m.p. 67.3° to 69.8° C., acid v. 17.5 to 23.8, sap. v. 77.5 to 83.7, and i.v. 21.6 to 28.8 (See Flax.)

**Ghedda** (Gedda, East Indian Wax), of m.p. at 55° to 56° C., is stated to contain about 48 per cent. ceryl alcohol, 7 per cent. hydrocarbons, and about 24 to 25 per cent. hydroxymargaric acid, together with some 8 to 9 per cent. palmitic acid, etc.

**Glyceria Wax** forms a coating on the stems of the Australian "cane grass" (*Glyceria ramigeria*); it resembles carnauba wax; is but little soluble in ether, has a high acid value and m.p. 82° C.

**Godang Wax** (Getah Wax) is made from the latex of a wild fig-tree (*Ficus ceruflua* or *F. subracemosa*). The wax from *F. variegata* is reported to consist of ficoceryl alcohol and ficoceric acid or beta-amyrol palmitate. It is soluble in hot alcohol.

**Japan or Vegetable Wax** (Tallow), or tree wax, is obtained in Japan, the East Indies, Indo-China, and Madagascar from berries of the *Rhus succedanea* and several species of sumach-tree by boiling the fruit in water. The kernels yield from 31 to 34 per cent. fat and the mesocarp 28.9 per cent. It is not a real wax but a glyceride, and contains palmitin with free palmitic acid. It is yellow, soluble in benzol and naphtha, of m.p. 53° C., sp. gr. 0.970 to 0.980, sap. v. 217 to 237.5, i.v. 5.9, and acid v. 10 to 25. The island of Kyushu accounts for about one-half of the total production from Japan. It is used in making soap, wax matches, candles, furniture polish, and leather-dressing. (See Sumac.)

**Lignocerin Wax** — See Tar (Beech-Wood).

**Montan Wax** is extracted from the bitumen of Thuringian lignite or from *pyropissite* (obtained from the lignite of Saxony and Bohemia) by a mixture of alcohol and benzene; said to contain as its chief constituent montanic acid ( $C_{28}H_{56}O_2$ ) of m.p.  $84.4^\circ C.$ , and another acid of m.p.  $89^\circ C.$  When refined by distillation with superheated steam it is white, and is used for candle-making and as a substitute for carnauba wax and ceresine; also for raising the melting-points of low-melting waxes, and in the making of gramophone and phonograph records. The refined wax melts at  $95^\circ$  to  $96^\circ C.$ , has sp. gr. of 1.00, sap. v. of 82.8; is soluble in benzol, chloroform, and carbon tetrachloride. The wax extracted from Irish peat and sold also as Montan wax is stated to be of a different character. It has a m.p. of  $76^\circ C.$ , an acid v. of 73, sap. v. 74, and an i.v. of 16 (Ryan and Dillon).

**Myrtle Wax** — See Bayberry Wax.

**Ocuba Wax** is obtained from the fruit of *Myristica ocuba officinalis*, which grows in marshy ground on the Amazon shores, and has a sp. gr. of 0.92, and m.p.  $39.4^\circ C.$ ; it is used in Brazil for making candles.

**Ozokerite Wax** — See Ceresine, and Ozokerite.

**Palm Wax** comes from the *Ceroxylon andicola*, a palm indigenous in the tropical parts of America, on the stem of which it forms a covering. In Ecuador, trees are found in great numbers, each of which furnishes about 50 pounds of wax. After washing with hot water, in which it does not melt, it is mixed with a little tallow and made into balls for exportation. It is yellow, and really consists of a wax and resin which can be separated by hot alcohol, the resin remaining in solution and the wax separating out as a jelly on cooling. When purified in this way it resembles beeswax in appearance and composition.

**Paraffin Wax**, like ceresine and ozokerite waxes, is not a true wax but is a high-melting hydrocarbon. It is usually prepared from petroleum, but may also be prepared from ozokerite and other materials by distillation or extraction. Refrigeration is commonly employed to separate paraffin from the petroleum fractions. (See "Wax Precipitation from Propane Solution," by Anderson and Talley (*Ind. Eng. Chem.*, 29, 432 (1937)).)

Paraffin is sold in various grades, depending on its melting point. These are all white, translucent, waxy solids, and are soluble in most organic solvents. The hardness and the uses to which paraffin is put depend on the melting point. Chief uses include the manufacture of candles, crayons, waxed paper, polishes, lubricants, and waterproofing materials.

**Pisang Wax**, a powdery mass obtained from the leaves of the *Cera musæ*, indigenous in Java.

**Raphia Wax** is found as a whitish layer on the under sides of the leaves of a Madagascar palm. The dried leaves yield about 10 per cent.; sp. gr. 0.834, m.p.  $82.5^\circ C.$ , sap. v. 51, and i.v. from 7.7 to 10.7.

**Rose Wax** — The constants of the crude wax have been given by H. Prophète as follows: m.p.  $61^\circ C.$ , sap. v. 29.8, i.v. (Hübl) 13, Reichert-Meisss v. 1.35, acid v. 3.15.

**Spermaceti** (Cetaceum, Cetin), consisting mainly of the esters cetyl myristate ( $C_{18}H_{37}\cdot COOC_{16}H_{33}$ ), and laurate ( $C_{11}H_{23}\cdot COOC_{16}H_{33}$ ), together with cetyl palmitate ( $C_{15}H_{31}\cdot COOC_{16}H_{33}$ ), which contrary to the common belief is present in relatively small proportion, is a pearly white, fatty substance found in certain cavities of the head of the sperm whale (*Physeter macrocephalus*) and in smaller quantity in the blubber of the *Balaena rostrata*. The crude material is apt to become rancid when exposed to the air and light, and is associated with sperm oil, from which it has to be freed before it attains the scaly, brittle, yet soft character of the commercial article. It is soluble in carbon disulphide and ether; has a sp. gr. of 0.945 to 0.960, sap. v. of 123 to 135, i.v. 3.5 to 6.7, and m.p.  $44^{\circ}$  to  $47.5^{\circ}$  C. It can be distilled at  $360^{\circ}$  C. without decomposition, and repeated crystallization gives, it is said, practically pure cetyl palmitate, melting at  $53^{\circ}$  C. By hydrolysis with aqueous-alcoholic potassium hydroxide it yields cetyl alcohol ( $C_{15}H_{31}CH_2OH$ ). It is exported from the United States and Japan, and amongst other applications is used in the manufacture of candles, soaps, and ointments. The Arctic sperm oil is also said to be a true wax, containing 43.2 per cent. unsaponifiable matter, consisting mainly (70 per cent.) of oleyl alcohol and cetyl alcohol. (See Whale Oils.)

**Sugar-Cane Wax**, a by-product extracted in Natal and Java in the sugar manufacture, obtained from the canes, particularly the violet species, by scraping or skimming off the juice resulting from boiling them out, or from the dried filter-press cake, using benzol as the solvent. It is hard, yellow, brown, or green, granular, soluble in hot alcohol and benzene; m.p.  $55^{\circ}$  to  $62^{\circ}$  C., sp. gr. 0.961, sap. v. from 168 to 177, and i.v. 60. It appears to contain about 45 per cent. of myricyl alcohol ( $C_{29}H_{59}CH_2OH$ ) and another substance ( $C_{30}H_{60}O_2$ ) associated with other constituents. It finds a ready market as a substitute for carnauba wax.

**Wool Fat** — This is a wax, but incorrectly called a fat. It is obtained from the wool of sheep, and when impure has a very offensive odour. It consists mainly of sterols and esters of sterols, and the purified product is used as an ointment base in pharmacy; when mixed with about half its own weight of water, with which it forms water-in-oil emulsion, it is known as lanoline, and as such is employed in cosmetics. The free alcohols obtained from wool fat are known as wool alcohols, and are used as emulsifying agents and in skin creams.

*References:* *The Chemistry and Technology of Waxes*, by A. H. Warth (Reinhold Publishing Corp., New York); *Commercial Waxes—Natural and Synthetic*, by H. Bennett, Editor (Chemical Publishing Co., Brooklyn); *Plastics, and Silicones*.)

**WEED DESTROYERS** — See Herbicides.

**"WEEDEX"** — A calcium chlorate weed destroying agent.

**WEIGHT** — The force by which the mass of a substance is attracted by gravity, varying with the altitude where determined. The force of 980 dynes is the weight of a mass of 1 gram. In common usage the term weight is used when it is understood that the comparison of masses is intended.

**WEIGHTS AND MEASURES** (see also **Hydrometers**) — The weights and measures used in chemistry are those of the International system, the units of which and their British and United States equivalents are as follows :

**Length** : The International Standard of length is the Prototype Metre of platinum-iridium at the International Bureau of Weights and Measures.

25.40 millimetres (mm.) = 1 inch (in.).

1 metre (m.) = 39.3700 inches.

1 kilometre (km.) = 1,000 metres = 1,093.61 yards.

1 decimetre (dm.) is the 10th part of a metre.

1 centimetre (cm.) is the 100th part of a metre.

1 millimetre (mm.) is the 1,000th part of a metre.

1 micron ( $\mu$ ) is the 1,000th part of a millimetre ( $10^{-3}$  mm., or  $10^{-4}$  cm.).

1 millimicron (m $\mu$ ) is one-millionth of a millimetre ( $10^{-6}$  mm., or  $10^{-7}$  cm.).

1 Ångström =  $10^{-7}$  mm. =  $10^{-8}$  cm. =  $10^{-10}$  m.

1 mile (mi.) = 1.609 kilometres (km.).

**Mass** : The International Standard of mass is the Prototype Kilogram of platinum-iridium at the International Bureau of Weights and Measures.

1 kilogram (kg.) = 1,000 grams (g.) (gm.) (grm.) (gramme) = 2.2046223 pounds avoirdupois.

1 gram = 15.4324 grains.

1 decigram (dg.) is the 10th part of a gram.

1 centigram (cg.) is the 100th part of a gram.

1 milligram (mg.) is the 1,000th part of a gram.

1 microgram ( $\mu$ g.) or 1 gamma ( $\gamma$ ) is the 1,000,000th part of a gram.

1 pound (lb.) = 453.59 grams, and 1 ounce = 28.35 grams.

1 metric ton = 2,204.6 pounds.

1 pound avoirdupois = 7,000 grains, and 1 pound troy = 5,760 grains.

1 stone = 14 pounds.

1 hundredweight (cwt.) (Brit.) = 112 pounds.

1 long (gross) ton = 2,240 pounds.

1 short (net) ton = 2,000 pounds.

**Capacity** : One litre equals the volume occupied by one kilogram of water at 4° C.

1 litre (l.) = 1,000 millilitres (ml.) = 1,000.027 cubic centimetres.

= 35.196 fluid ounces (Brit.) = 1.7598 pints (Brit.).

= 33.814 fluid ounces (U.S.A.) = 1.0567 quarts (U.S.A.).

1 millilitre = 16.894 minims (Brit.) = 16.231 minims (U.S.A.).

1 dekalitre (10 litres) = 2.20 gallons (Brit.) = 2.64 gallons (U.S.A.).

1 hectolitre (100 litres) = 22.0 gallons (Brit.) = 26.4 gallons (U.S.A.).

1 British gallon = 70,000 grains = 10 pounds avoirdupois of water at 62° F. = 4.5460 litres = 277.276 cubic inches.

- 1 United States gallon=8·337 pounds avoirdupois of water at  
 60° F.=3·7853 litres=231 cubic inches.  
 1 cubic foot water at 60° F.=62·37 pounds.

**Apothecary Weights :**

- 20 grains=1 scruple.  
 60 grains=3 scruples=1 drachm.  
 480 grains=8 drachms=1 ounce.  
 12 ounces=1 pound.

**Troy Weights :**

- 24 grains (gr.)=1 pennyweight (dwt.).  
 480 grains=20 pennyweights=1 ounce.  
 12 ounces=1 pound.

**Domestic Capacities :**

- 60 minims=1 fluid drachm (fl. drm.) =1 teaspoonful.  
 120 minims=2 fluid drachms=1 dessertspoonful.  
 240 minims=4 fluid drachms= $\frac{1}{2}$  fluid ounce (fl. oz.)=1 table-  
 spoonful.  
 20 fluid ounces=1 pint (O.).  
 8 pints=1 gallon (C.).

**Square Measure :**

- 144 square inches=1 square foot.  
 9 square feet=1 square yard.  
 30 $\frac{1}{4}$  square yards=1 rod, pole, or perch.  
 40 perches=1 rood.  
 4 roods=1 acre.  
 640 acres=1 square mile.

**Square Metric Measure :**

- Milliare=0·1 square metre.  
 Centare=1·0 square metre.  
 Deciare=10·0 square metres.  
 Are=100·0 square metres.  
 Decare=1,000·0 square metres.  
 Hectare=10,000·0 square metres.  
 (1 sq. metre=1·196 square yards, and 1 square centimetre=  
 0·155 square inch.)

**Cubic Measure :**

- 1,728 cubic inches=1 cubic foot.  
 27 cubic feet=1 cubic yard.

**WEIZMANN'S PROCESS** — See Acetone.

**WELDING : ITS CHEMICAL ASPECTS** — Apart from other applications, the subject of welding is important in respect of the storage of gases, including oxygen, chlorine, ammonia, sulphur dioxide, and phosgene, in welded cylinders and tanks. The welded seams involve risks not experienced in solid drawn vessels. Steel used for welding in chemical and process industries should have a carbon content below

0.25 per cent. as being the most easily handled. Drums built by electric or oxy-acetylene welding of a safe and lasting character are commercially available.

(See "Designing Welded Chemical Equipment," by W. Spraragen (*Ind. Eng. Chem.*, **29**, 366 (1937)); Argon; Oxy-Acetylene Flame, and "Thermit" Process.)

**"WELDON" CHLORINE PROCESS** — See Chlorine, and Manganese.

**WELSBACH LIGHT** — See Thorium.

**"WESTORAN"** — A proprietary emulsifiable hydrocarbon, miscible with water, for use as a solvent scourer for cotton and other fabrics, and as an insecticide.

**"WESTROL"** — A proprietary article described as a combination of high-class oils with a non-inflammable solvent (trichlorethylene); soluble in water; for use as a solvent scouring agent for cotton fabrics. A similar article named "Westrosol" or "Tri" is for use in respect of woollen fabrics and general washing purposes.

**WETTING AGENTS (Wetters, Spreaders)** are preparations used as constituents of spraying fluids and emulsifiers to facilitate their spreading, and of dyeing liquids to enable the dye to reach every spot of the fibre at the same time. Agents used are soap, sulphated castor oil, sulphonated naphthols, "Gardinol," "Mercerol," "Nacconol," "Areskap," and other proprietary materials.

Salts, amides, ester-amides, or esters of high molecular organic acids used as wetting agents are improved by incorporation with wetting agents of the sulphonic acid type. Examples are said to be beta-diethylaminoethylamide of oleic acid and sodium propylnaphthalene sulphonate; stearamide and sulphonated oleic acid; oleic beta-hydroxyethylamide or anilide, or cyclohexylamide and diisopropylnaphthalene sulphonic acid.

*References*: "Resistance of Solid Surfaces to Wetting by Water," by R. N. Wenzel (*Ind. Eng. Chem.*, **28**, 988 (1936)); Colloidal State, Lubricants, Ores, and Surface Tension.

**WHALE OILS** — The sp. gr. ranges from 0.877 (from head cavities of sperm whale) to 0.923 (from blubber of humpback); ref. ind., 1.463 (from head cavities of sperm whale) to 1.475 (from blubber of humpback); sap. v., 127 (from blubber of sperm whale) to 199 (tongue of humpback); acid v., 0.75 (from blubber of sei whale) to 5.8 (blubber of humpback); i.v., 0.66 (from head cavities of sperm whale) to 119 (blubber of humpback).

The oil from the humpbacked whale is reported to contain about 10 per cent. of saturated acids (chiefly palmitic and myristic), and not more than 15 per cent. of highly unsaturated acids, the remainder consisting of members of the oleic acid series. Of the simple unsaturated acids of the oleic acid series, the chief are oleic acid and one with the composition  $C_{16}H_{30}O_2$ , together with an isomeride of erucic acid. The oil from the finner whale has a higher iodine value; contains about 25 per cent. saturated acids, and not more than 15 per cent. highly

unsaturated acids, the remainder being members of the oleic series. Zoomaric acid  $(CH_3(CH_2)_5CH:CH(CH_2)_6COOH)$  is said to occur in sei whale oil. After removal of the oil the residual material can be used as a fertilizer or cattle food. The Sixty-Third Annual Report of the New Zealand Dominion Analyst gives analytical results concerning New Zealand whale oils as follows: Acid v. ranging from 5.3 to 14.8; sap. v. 190 to 191.7; i.v. 134.8 to 140.5; ref. ind. at 40° C. 1.4655 to 1.4662; ref. ind. at 60° C. 1.4575 to 1.4588; and sp. gr. 0.923 to 0.925. These oils differ from Antarctic whale oils in throwing down hardly any stearine when chilled. (See Fish Oils, and Oils.)

**WHEAT (and Bread)** — Cereal grasses of the genus *Triticum*, the common wheat being *T. vulgare* or *sativum*. The flour from wheat and other cereals varies in proportions of nitrogen content, gluten (consisting of gliadin and glutenin), soluble extract (including a small proportion of oil), soluble phosphates, acidity, diastatic capacity, swelling properties of the contained hydrogels, etc. The following analyses of cereals are given in one report:

	Fat %	Proteins %	Carbo- hydrates %	Ca %	P %	Ca/P ratio
Oatmeal ..	7.2	16.1	67.5	0.069	0.392	1 : 5.7
Barley ..	1.1	8.5	77.8	0.020	0.181	1 : 9.0
Rice ..	0.3	8.0	79.5	0.009	0.096	1 : 10.7
Wheat flour (white) ..	1.4	7.9	76.4	0.020	0.092	1 : 4.6
Wheat germ	7.7	21.4	51.1	0.071	1.050	1 : 14.8

Another report gives the following as average values:

	Fat %	Protein %	Cellulose or Crude Fibre %	Ash
Wheat ..	2.10	12.00	2.20	1.80
Flour ..	1.25	11.00	0.25	0.40
Bran ..	3.60	15.40	9.00	5.80

English wheat contains from 13 to 14 per cent. water, 2.35 to 2.85 per cent. oil, 12.19 per cent. albuminoids, 68 to 69 per cent. digestible carbohydrates, 1.30 to 1.75 per cent. woody fibre, 1.7 to 1.8 per cent. mineral matter (Smetham and Dodd).

Wheat bran constitutes 13.5 per cent. of the grain and has a protein content of 15 to 17 per cent.; weight for weight it contains two to three times as much of the necessary amino-acids for nutrition as the endosperm (white flour).

Bread is baked dough charged variously with yeast for leavening or some baking powder to produce gas, in order to distend it and make it more digestible. As made from flour it is a prime foodstuff.

An 80 per cent. "patent" flour is one in which the refining has been carried on so that 80 per cent. of the total flour recovery from the grain is in the final product and only 20 per cent. left in the second-grade flours. It is stated that wheat usually yields about 70 per cent. total flour and 30 per cent. feeding stuff, such as bran and shorts. Of this 70 per cent. total flour about 80 per cent. goes into "patent" flour as already described, about 15 per cent. into "first clear," and 5 per cent. into other fractions. It has been shown that the digestibility of that made from 80 per cent. flour is practically as good as that made from 70 per cent. flour, while the difference between the digestibility of breads made from 80 and 90 per cent. flours may be represented as follows :

	80 Per Cent. Bread	90 Per Cent. Bread
Energy .. .. .	96.14	94.5
Proteins .. .. .	89.40	87.3

In other words, the digestibility is only about 2 per cent. less in the 90 per cent. flour, while there is a gain of 10 per cent. in quantity.

**Fumigation** — Ethyl acetate is a safe and effective fumigant for wheat at shipping terminals, where it is inadvisable to use carbon disulphide. Ethylene oxide is also said to be an efficient agent, but, according to Roark and Cotton, ethylene dichloride with carbon tetrachloride in ratio 3 : 1 by volume at rate of 6 pounds per 1,000 cubic feet of stored grain appears to be the best fumigant.

The **bleaching** of flour by chemical reagents such as chlorine, nitrous acid, nitric peroxide, nitrogen trichloride, benzoyl peroxide, and persulphates is attributed to the formation of colourless derivatives of carotene (the yellow colouring matter of the endosperm), and is stated to be attended with some loss of its vitamin A content, but not destructive of the B variety. When chlorine is used alone or with  $\frac{1}{2}$  per cent. nitrosyl chloride, from  $\frac{1}{2}$  to 2 ounces per sack of 280 pounds flour is employed, but the common practice is the employment of from 2 to 5 grams of nitrogen trichloride per sack of flour.

*References :* *Wheat and Its Products*, by A. Millar ; *Modern Cereal Chemistry*, by D. W. Kent-Jones (Northern Publicity Co.) ; *Chemistry of Wheat Flour*, by C. H. Bailey (Reinhold Publishing Corp., New York) ; *Chemistry of Bread-making*, by J. Grant (E. Arnold and Co., London) ; and *Bread-making : its Principles and Practice*, by E. B. Benion (Oxford University Press) ; *Wheat and Flour Quality*, by C. O. Swanson (Burgess Publishing Co., Minneapolis) ; *The Constituents of Wheat and Wheat Products*, by C. H. Bailey (Reinhold Publishing Corp., New York) ; and *Yeasts*.

**WHEY** — See Lactose, and Milk.

**WHISKY** — A spirit distilled from a mash of cereal grains saccharified by the diastase of malt, and subsequently fermented by the agency of yeast. Rye and corn (Bourbon) whiskies are two common types: Scotch whisky is made from fermented malted cereal, and Irish from a mash of malt and cereals. Whisky contains about 40 per cent. of ethyl alcohol

and small quantities of higher alcohols, esters, and organic acids, also traces of aldehydes. (See "Changes in Whiskey Stored for Four Years," by P. Valaer and W. H. Frazier (*Ind. Eng. Chem.*, 28, 92 (1936)).)

**WHITE ARSENIC** — Arsenious oxide. (See Arsenic.)

**WHITE DAMP** — See Carbon (Oxides).

**WHITE GOLD** — An alloy of 60 parts of gold and 40 parts by weight of platinum which resists nitric acid and is much used in the jewellery trade.

**WHITE LEAD** — See Lead (White-Lead).

**WHITE METAL** — A classification covering alloys of antimony-base, lead-base, or tin-base type, such as bearing metals, type metals, and babbitt metal. (See *Metallurgy of White Metal Scrap and Residues*, by E. R. Thews (Chapman and Hall, London); and Alloys.)

**WHITE VITRIOL** — A commercial name for zinc sulphate.

**WHITWASH** — Slaked quicklime made into a suspension or milk with water.

**WHITING** — A finely pulverized preparation of chalk purified by washing; used in making polishing and scouring materials, distemper paints, putty, aerated waters, and in the rubber and oilcloth industry.

**WIJS' NUMBER** — See Fats.

**WILKINITE** — A Wyoming deposit of similar character to bentonite. (See Bentonite.)

**WINE** — The fermented juice of grapes (of which there are some 600 varieties), the colour depending upon that of their husks if and when they are included in the making. Red grapes can be made to give yellow or white wines if the husks be excluded, as in the cases of sherry and champagne. Portugal is famous for port; Spain for sherry; Germany for hock and moselle; Italy for capri and chianti; France for claret, burgundy, chablis, sauterne, and champagne; Greece and Spain for malmsey; while good wines are also produced in Australia, South Africa, California, etc.

The flavour and other characters of wines depend not only upon the kind of grapes from which they are made, but also upon the soil on which they are grown and upon the ethereal bodies resulting from changes that take place upon keeping. Dry wines contain little or no grape sugar; sweet wines contain sugar in greater or less proportion; while effervescent wines like sparkling moselle and champagne contain sugar in a state of fermentation, or are effervescent as the result of fermentation that takes place after bottling. They all contain alcohol as a natural product of the fermentation by which they are produced (the ferments consisting of the living organisms contained in the so-called "bloom" of the husks), together with, in many cases, small quantities of sugar, acids (including tartaric acid), colouring matters, and so-called extractive matters of indefinite composition. Old wines, particularly port, deposit potassium acid tartrate upon long keeping. (See Tartar.)

Alcohol is added to many wines, such as port and sherry, and some of the Australian and Californian wines, in order to "fortify" them, as it is termed, against the acetic change that might otherwise subsequently take place of the smaller natural content of alcohol. The alcoholic strength of wines is by no means constant, but as sold it may be said that port contains from 14 to 23 per cent.; sherry from 14 to 18 per cent.; claret from 6 to 12 per cent.; hock and other light wines from 5 up to 8 per cent.; beer, 5 to 6 per cent.; small beer, 2 per cent. (See Beer, and Yeasts.)

It is said that to produce good wines, the grape juice must contain not less than 20 per cent. glucose, and not infrequently sugar is added to the "must" (expressed juice of the grapes).

*References:* *Origin, Nature, and Varieties of Wine*, by Thudichum and Dupré (Macmillan and Co., London); *The Chemistry of Wine-making*, by J. T. Hewitt (H.M. Stationery Office, 1928); *Report on the Composition of Some of the Commoner British Wines and Cordials* (H.M. Stationery Office); and Wine Symposium in *Ind. Eng. Chem.*, 27, 1235 (1935).

**WINTERGREEN (OIL OF)** — See Gaultheria Oil, and Methyl Salicylate.

**WITCH HAZEL LEAVES** — See Hamamelis.

**WITHERITE** — Mineral barium carbonate ( $\text{BaCO}_3$ ), of crystal system No. 4, and sp. gr. 4.3.

**WOAD** — Blue colouring matter prepared from the leaves of *Isatis tinctoria* (Dyer's Woad, I. *tinctoria*), which contains indican and is chemically identical with indigo. The leaves after partial drying are pounded into a paste and allowed to ferment preparatory to extraction of the colouring matter thus produced.

**"WOLFEN"** — German designation for the fungicide, copper dimethyldithiocarbamate.

**WOLFRAM** — See Tungsten. Wolfram is the name of the element accepted (1949) by the International Union of Chemistry. Optional (1951) for British and American chemists.

**WOLFRAMITE** — See Tungsten.

**WOLLASTONITE** — A natural calcium silicate ( $\text{CaSiO}_3$ ), of crystal system No. 5, and sp. gr. 2.7 to 2.9.

**WOOD** — Wood consists of a mass of cells possessed of walls and containing a great variety of substances, such as ligno-cellulose (the fundamental constituent), starch, resinous matters, essential oils, etc. (See J. M. Maby on its structure (*Analyst*, 57, 2 (1932)).) By some, it is thought probable that lignin and carbohydrates are contained in the wood as glucoside-like compounds, and that in the sulphite-boiling process (see Paper) these are hydrolysed, soluble calcium lignin sulphites being thereby produced.

The greatest forest reserves of hard and soft woods are those of northern Europe and northern Asia, the Pacific slope and Rocky Mountain regions of western North America, eastern Canada and

the United States, the territories in the Gulf of Mexico region, and the tropical forests of Central and South America, central Africa, and the Far East. See *Forest Resources of the World*, by R. Zon and W. N. Sparhawk (McGraw-Hill Book Co., New York).

In England a seedling tree doubles its size in two years, and at twenty years a good growing larch will increase as much as 20 per cent. in the following year, while at forty years the percentage growth will still be about 6 per cent. per annum. In America, the rate of forest growth is very rapid in Oregon, Washington, and British Columbia.

The following table of analyses of certain American woods is taken from a published paper by G. R. Ritter and L. C. Fleck:

ANALYSES OF CERTAIN AMERICAN HARD AND SOFT WOODS ON MATERIAL DRIED AT 105° C.

	Western Yellow Pine	Yellow Cedar	Incense Cedar	Red- wood	Tanbark Oak	Mes- quite	Balsam	Hickory
Ash .. ..	0.46	0.43	0.34	0.21	0.63	0.54	2.12	0.69
Soluble in cold water ..	4.09	2.47	3.64	7.36	4.10	12.62	1.77	4.78
Soluble in hot water ..	5.05	3.11	5.38	9.86	5.60	15.09	2.79	5.57
Soluble in ether ..	8.52	2.55	4.31	1.07	0.80	2.30	1.23	0.63
Soluble in 1 per cent. NaOH solution ..	20.30	13.41	17.69	20.00	23.96	28.52	20.37	19.04
Acetic Acid ..	1.09	1.59	0.91	1.08	5.23	2.03	5.80	2.51
Methoxy content ..	4.49	5.25	6.24	5.21	5.74	5.55	5.68	5.63
Pentosan ..	7.35	7.87	10.65	7.80	19.59	13.96	17.65	18.82
Methyl-pentosan ..	1.62	3.42	1.35	2.75	None	0.70	0.86	0.80
Cellulose ..	57.41	53.86	41.60	48.45	58.03	45.48	54.15	56.22
Lignin ..	26.65	31.32	37.69	34.21	23.85	30.47	26.50	23.44

An analysis of spruce wood gives the cellulose content (free from pentosans) to be 53 per cent., that of hemi-cellulose as 15 per cent., lignin 30 per cent., and other substances 2 per cent.; while E. Hägg-lund gives the constituents of pine wood as cellulose about 42 per cent. polysaccharides 24 per cent., lignin 28 per cent., acetic acid 2 per cent and rosin, ash, and protein, etc., about 4 per cent.

The results of a published analysis of oak wood (*Quercus agrifolia*) are as follows:

	Per Cent.
Loss on drying .. ..	4.20
Benzene extract .. ..	0.50
Alcohol extract .. ..	4.33
Water extract .. ..	3.66
Soluble in cold 5 per cent. sodium hydroxide solution	18.71
Cellulose .. ..	45.48
Lignin .. ..	20.25
Pentosans not otherwise accounted for .. ..	1.89
Mannan (residual) .. ..	None
Galactan (residual) .. ..	1.49

100.51

The wood of a deciduous tree (aspen) gave upon a recorded analysis : ash, 1.03 per cent. ; fats and resins, 1.07 per cent. ; methoxyl ( $\text{OCH}_3$ ), 6.02 per cent. ; pentosan, 17.61 per cent. ; lignin, 26.42 per cent. ; cellulose, 51.61 per cent. ; galactan, 0.99 per cent.

Green wood contains from 40 to 60 per cent. water, and ordinary dried woods contain about 50 per cent. carbon, 6 per cent. hydrogen, 40 to 42.5 per cent. oxygen, 1 per cent. nitrogen, and yield from 0.81 to 3.37 per cent. ash.

Wood can be completely dissolved by heating at 75° C. in acetic anhydride and zinc chloride, coupled with passage of chlorine through the mixture, and from examination of the product resulting from pouring into water, H. Urban has found that the composition of wood agrees with the assumption that it consists in the main of 70 per cent. cellulose and 30 per cent. lignin.

The wood from various species of trees varies in structure, specific gravity, elasticity, and strength. The following table gives the average specific gravities of various woods :

Cork .. .. .	0.240	Mahogany (Spanish)	0.720
Poplar .. .. .	0.384	Pine (pitch) ..	0.736
White pine .. ..	0.39 to 0.456	Maple .. .. .	0.752
Yellow pine .. ..	0.448	Hornbeam .. ..	0.761
Larch .. .. .	0.51 to 0.53	Yew .. .. .	0.788 to 0.808
Mahogany (Honduras)	0.560	Birch .. .. .	0.793
Cedar (United States)	0.561	Ash .. .. .	0.845
Willow .. .. .	0.585	Beech .. .. .	0.852
Chestnut .. .. .	0.610	Red gum (eucalyptus)	0.901
Birch (United States)	0.648	Logwood .. ..	0.913
Sycamore .. .. .	0.624	Cedar (Canadian)	0.910
Teak .. .. .	0.660 to 0.750	Oak (English)	0.934
Walnut .. .. .	0.671	Oak (African)	0.944
Oak (United States)	0.672	Blue gum (eucalyptus)	1.100
Elm .. .. .	0.673	Ebony .. .. .	1.208 to 1.331
Pine (red) .. ..	0.673	Box .. .. .	1.328

The next table, giving the coefficients of absorption, is taken from an article by D. M. Newitt in the *Chemical Age* of August 26, 1922 :

COEFFICIENTS OF ABSORPTION (GRAMS PER CUBIC CENTIMETRE  $\times 10$ )

Liquid	Cypress	Fir	Pine	Redwood	Maple	Oak
Water .. .. .	2.3	3.1	3.0	3.6	5.4	4.0
Hydrochloric acid ..	2.3	2.6	2.4	2.8	4.2	3.6
Sulphuric acid .. ..	2.2	2.0	3.1	3.1	4.1	2.6
Nitric acid .. .. .	2.2	2.7	2.3	2.8	4.8	3.8
Caustic soda .. .. .	4.0	5.7	4.3	6.0	5.7	7.0
Sodium carbonate ..	2.0	3.6	2.5	4.2	4.2	2.4
Bleaching powder ..	1.5	2.0	1.3	3.1	3.9	1.6
Sodium bisulphite ..	3.6	3.3	1.8	4.4	4.4	2.5
Sodium chloride .. .	1.0	1.6	1.2	3.1	3.5	1.3
Turpentine .. .. .	2.5	1.6	0.7	3.1	1.9	0.7
Linseed oil .. .. .	1.2	2.0	1.0	3.0	1.6	1.0

To quote his words, "For any particular liquid there is always some wood which is particularly resistant to that liquid, and which should be selected for building the tank. Caustic soda and nitric acid are exceptions to this generalization; they cannot satisfactorily be stored in wood. The same applies to most hot alkaline and acid liquids."

*References*: "Resistant Woods" in *Chemical and Metallurgical Engineering*, 1929, 567; wood as a chemical raw material, by F. Bergius in *Ind. Eng. Chem.*, 29, 250 (1937); conference on "The Fire-Proofing of Timber" in *C.T.J.*, 90, 307 (1932); the identification of wood by chemical means in *Analyst*, 57, 101 (1932); *The Nature of the Chemical Components of Wood*, edited by C. J. West (Tech. Assoc. Pulp and Paper Ind., New York); *Wood Chemistry*, by Louis E. Wise (Reinhold Publishing Corp., New York); Paper, and Wood Pulp.

**Decay** — All woods are more or less liable to the attacks of fungi and the decomposition known as dry rot; heat, air, and moisture being necessary for the growth of all dry-rot fungi, which, however, will not thrive in the presence of a great excess of any of these agencies. In this change, the proportions of carbon and hydrogen contained in the wood are reduced by the production of carbon dioxide and water. It is largely one of slow oxidation, accompanied by a loss of density, until the wood, as in the case of trunks of trees hollowed by decay, becomes rotten.

The fungi *Polyporus hybridus* and *Melaphora puteana* are, according to one account, held responsible in the main, but more than seventy different kinds have been isolated from wood and wood pulp, and the ravages of many forms of insect life are involved in the general destruction. Coniferous timber affected by the blue-stripe fungus, *Ceratosomella*, is not infrequently used for building, under the wrong impression that the appearance is due to sap-wood.

The fungi responsible for the decay of wood may be said to consist of two classes, namely, the dry-rot type, which flourishes within a narrow range of temperature (cold to moderate) and does not require any great amount of moisture; and the damp-rot type, which thrives in warmer temperatures and requires much moisture. Among the common wood-destroying fungi are *Lenzites trabea*, *L. lepideus*, *Fomes roseus*, *L. sæpiaria*, *Merulius lacrymans*, and *Coniophora cerebella*, the last-named being the organisms which cause dry-rot more frequently in worked timber out of doors than inside buildings. In spruce, hemlock, balsam, and aspen, the progress of decay is indicated by a decrease in the percentage of stable cellulose and increase in that of lignin; ultimately, at least 50 per cent. of the lignin is converted into humic acid.

According to Barton-Wright and Boswell, the *Merulius lacrymans* removes the galactin, mannan, and cellulose fractions from spruce, while the hemi-celluloses and lignin are not affected, and there is no delignification of the woody tissue.

Furniture and the woodwork of houses are also liable to attack by the larvæ of certain beetles, among which are the common furniture beetle *Anobium punctatum* De J., while the Death-watch beetle,

*Xestobium rufovillosum* De J., more usually attacks the timber (particularly oak) of old houses, and the powder-pest beetle (*Lyctus*) mostly affects sap-wood (new furniture and sawn timber). Heat-treatment is the best remedy when applicable; otherwise, fumigation with a fungicidal vapour such as formaldehyde, or, better still, the application by spray or otherwise, of properly diluted solutions of powerful agents such as "Okol," creosote, carbon tetrachloride, dichlorobenzene, chlorinated naphthalenes, and copper sulphate to the surfaces, joints, and cracks. (See *Enemies of Timber*, by E. G. Blake (Chapman and Hall, London); publications of the U.S. Forest Products Laboratory, Madison, Wisconsin, U.S.A., a list of which will be sent upon request; and Fungicides.)

With respect to **moisture-proofing** of wood, aluminium leaf-proofing has been advocated as providing the best protection as compared with oils, varnishes, asphalt, paints, etc.

**Preservation** — For the protection of wood from moisture, asphalt and pitch paints are efficient, while aluminium leaf can be used for large, unbroken surfaces such as aeroplane propellers; various lacquers, varnishes, and vaseline smeared over varnish, are also available for certain applications. Creosote is largely used as a general wood and fence preservative. The quality of b.p.  $210^{\circ}$  to  $355^{\circ}$  C., with a sp. gr. of 1.09 at  $20^{\circ}$  C., is ordinarily regarded as good for railway sleepers, used at  $178^{\circ}$  F., employing from 15.6 to 18.7 pounds per cubic foot of timber under reduced pressure, the wood being first dried by stacking.

Zinc chloride (used with or without creosote) and petroleum oils are also used in respect of railway sleepers.

The impregnation of dried wood with cold solution of mercuric chloride is alleged to give permanent preservation with 2 or 3 per cent. of the salt, although it is only absorbed and does not enter into combination with the wood substance, but it is expensive and its poisonous character makes its use very dangerous. (See Kyanizing.)

Impregnation with sulphur can at times be usefully employed for wood preservation. Experiments with a medium petroleum distillate containing a small proportion of an organic arsenical compound have proved resistant to the attacks of *teredo* and *limnoria* over a period of four years.

A preservative named "Ac-zol" is claimed to have all the advantages without the objections of some of the older preservatives, and is made up of ammonium salts, copper and zinc salts, and phenols. It is said to be readily absorbed, exhibits good antiseptic and insecticidal properties, and should be used in the proportion of 6 or 8 parts with 94 or 92 parts of water, applied by immersion, vacuum-pressure treatment, or by the brush. It contains 150 times the percentage of phenols and 10 times the percentage of metallic salts required to sterilize gelatine (which substance is more liable to fungoid attack than ligneous matter), and the compound is claimed to fix the phenols constituting the active constituents of creosote.

Many preparations have been tested for protection against the *Lyctus* beetle and the Death-watch beetle in timbers, one such being a water

emulsion of zinc or barium oleate 3, cedar-wood oil 3, soap 1, paraffin wax 10, and water 83 parts. Where colour is not important, copper oleate may be used and a volatile poisonous insecticide such as dichlorobenzene added. "Okol" properly diluted is also effective.

To strengthen decayed timber and at the same time to carry a permanent poison and evolve a penetrating vapour, cellulose acetate, fluosilicates, hard waxes, and silicon esters are among the materials that have been more or less used.

A solution of 1 per cent. sodium fluoride and 0.66 per cent. mercuric chloride is of value for the prevention of mould formations in wood.

Pentachlorophenol is an effective preservative when used in oil, as is also its sodium salt.

For the protection of mine timber against fungi, a 5 per cent. solution of zinc sulphate under pressure is sometimes used; whilst old oak may be protected against the attacks of worms and beetles by impregnation with a mixture of two parts linseed oil and one part turpentine oil.

In the "Cobra" method of wood preservation the preservative liquid, consisting of an aqueous solution of sodium fluoride, sodium dinitrophenoxide, and some zinc chloride, is injected through boreholes several centimetres deep.

A novel method is that of impregnation of the wood with synthetic resins in liquid form, which is said to fill all the interstices and cells, and causes coagulation of the albuminous content, thus rendering it impervious to bacteria, fungi, etc.

*References:* *A Treatise on Wood Preservation*, edited by F. Mähle (Julius Springer, Berlin); *A Century of Wood Preserving*, edited by H. Boulton (P. Allen and Co., London); "Comparative Efficiencies of Components of Creosote Oil as Preservatives of Timber," by F. H. Rhodes and F. T. Gardner in *Ind. Eng. Chem.*, **22**, 167 (1930); marine piling investigation by U.S. Chemical Warfare Service in *Bull. Amer. Railway Eng. Assoc.*, **28**, No. 290 (1926); Reports of the Forest Products Research Board (H.M. Stationery Office); Reports of the Forest Products Laboratory, Madison, Wisconsin, U.S.A.

**Distillation** — The destructive distillation or carbonization of wood is conducted in iron retorts, yielding four primary products (in addition to the gases which are generated), namely, charcoal (left behind in the retorts), which can be used in making briquettes or otherwise utilized; acetic acid (recovered as acetate of calcium from the pyroligneous acid contained in the "green-liquor" or watery distillate), methyl alcohol, and tar.

The gases consist of about 15 per cent. hydrogen, 11 per cent. methane, 26 per cent. carbon dioxide, 41 per cent. carbon monoxide, and 7 per cent. hydrocarbons, and can be utilized for heating the boilers and the retorts. Wood tar is more complicated in character than coal tar, seventeen phenolic constituents having been identified, also numerous acids, aldehydes, ketones, lactones, aliphatic and aromatic hydrocarbons. Some details regarding pinewood tar will be found under the heading of Tar. Wood creosote is obtained from the distillation of the tar. (See Creosote (Wood).)

Wood rich in resin, such as that from pine trees, yields also turpentine, and by pushing the distillation further, the resin contained in the wood yields :

Rosin spirit distilling between	80°	and	150°	C.
Rosin pine oil	„	„	175°	„ 250° C.
Blue rosin oil	„	„	250°	„ 400° C.

Hard woods are almost exclusively used in the Canadian industry, as they yield higher percentages of acetic acid and methyl alcohol than the soft varieties.

In the Stafford process of wood distillation advantage is taken of the exothermic reaction that occurs when wood is somewhat heated.

See Dumesny and Noyer on *Wood Products* (Ernest Benn, London) ; H. M. Bunbury on *The Destructive Distillation of Wood* (E. Benn, London) ; M. Klar on *The Technology of Wood Distillation*, translated by A. Rule (Chapman and Hall, London) ; L. F. Hawley on *Wood Distillation* (Reinhold Publishing Corp., New York) ; *British Hardwoods : their Structure and Identification*, by L. Chalk and B. J. Rendle (H.M. Stationery Office) ; Alcohols (Methyl), Cellulose, Glucose, and Paper.

According to Campbell and Booth, air and kiln **drying** of wood decreases the total pentosans, but increases the cellulose-pentosans, and the lignin soft woods can be kiln-dried more easily than hard woods because of their lower pentosan content. An apparatus has been devised for automatically controlling the kiln, the action being dependent upon the change of weight of one of the boards of the stack being dried.

Wood of any kind can be **softened** by saturation with an aqueous solution of any kind of soap, and there is a patented process for producing in this way from fir, spruce, and alder a substitute for Florida cedar wood for making pencils.

Great advances in the use of wood have come about through the finding of synthetic plastics as adhesives for thin sheets of wood (plywood). (See "Plywood for War," by Thomas D. Perry (*Chemical and Engineering News*, 22, 700 (1944)) ; "Comparison of Methods for Improving Wood," by Louis Klein and others (*Ind. Eng. Chem.*, 36, 252 (1944)).) **Densified** wood is thus produced by impregnating layers of wood with phenol-formaldehyde resin, conditioning to allow penetration of the resin, and highly compressing the veneer layers to approximately one-half their original thickness. It is then tough, strong, resistant to water, chemicals, abrasion, and a wide range of temperature ; can be machined, and buffing produces a high gloss finish. Its density is approximately 1.3, and its dimensions remain permanent. (See "Arboneeld.")

**Uses** — Wood flour finds a number of industrial applications, being used in the making of linoleums, of dynamite (as an absorbent for the nitroglycerine), as a filler in plastic products, the making of Sorel cement, and as an application in the way of flecks on certain wall-papers, etc.

Wood is used and wood waste is utilized to some extent for the production of gas, glucose, alcohol, and otherwise (see *Ind. Chem.*, 8, 114

(1932) (Sawtelle process)); Auden and Joshua on the " Saccharification of Wood " (*J.S.C.I.*, 51, 11 T (1932)). According to M. Naphtali dried wood waste gives a yield of 60 to 70 per cent. of its carbohydrate content in sugar and a yield of 30 per cent. of its weight in lignin when treated on the counter-current principle with concentrated hydrochloric acid; and a process has been devised for the preparation of carbohydrate feeding stuffs from it.

In some places, for example, Oregon, Washington, and British Columbia, sawmill wood waste is an important industrial fuel for the generation of steam, using a large Dutch oven type of furnace.

**WOOD FIREPROOFING** — See Fireproofing.

**WOOD FLOUR** — As prepared from sawdust or pounded wood by special types of mills or grinding machines, this material is largely used as a "filling" in linoleum making; as a constituent of dynamite (being highly combustible and an excellent absorbent of nitroglycerine); also in the making of "Bakelite"; as a surfacing material in the making of velvet wall-papers, and as a non-breakable material in making of dolls, various toys, and other articles.

**WOOD OIL** — See Tung Oil.

**WOOD PULP** is prepared for use in the manufacture of paper and artificial silk by a number of processes—"mechanical," "semi-chemical," "sulphite," "sulphate" (actually sulphide) ("Kraft"), and "soda"

**WOOD PULP (MECHANICAL, DRY) EXPORTED AND IMPORTED BY COUNTRIES FOR THE YEAR 1936**

Authority: *International Trade in Certain Raw Materials and Foodstuffs* (League of Nations)

Data arranged and rounded off by the Editor.

EXPORTED BY			To	Metric Tons
Finland	..	..	United Kingdom	220,200
			United States	26,900
Norway	..	..	United Kingdom	192,800
			France	42,200
			Belgium-Luxemburg E.U.	36,200
Sweden	..	..	United Kingdom	187,200
			France	67,900
			United States	20,300
Canada	..	..	United States	154,500
WORLD'S EXPORTS REPORTED			..	1,028,300
WORLD'S IMPORTS REPORTED			..	1,048,400

(actually caustic soda), all of which (except the first) are directed to obtain the constituent cellulose dissociated more or less from its accompanying substances, the lignin being at the same time chemically dissolved. It is susceptible of attack by some seventy organisms, against which measures of protection have to be observed. (See *The Chemistry of Pulp and Paper Making*, by E. Sutermeister (John Wiley and Sons, New York); *Modern Pulp and Paper Making*, by G. S. Witham, Sr. (Reinhold Publishing Corp., New York); Fungicides, Paper, and Wood (Preservatives).)

The bleaching of mechanical wood pulp by the use of sodium peroxide substantially extends the use of this paper-making material. (See *Chemical and Engineering News*, 22, 332 (1944).)

**WOOD PULP\* (CHEMICAL, DRY) EXPORTED AND IMPORTED BY COUNTRIES  
FOR THE YEAR 1936**

Authority : *International Trade in Certain Raw Materials and Foodstuffs*  
(League of Nations)

Data arranged and rounded off by the Editor.

EXPORTED BY			To	Metric Tons
Sweden	..	..	United States	900,300
			United Kingdom	302,600
			France	183,700
			Germany	85,800
			Italy	79,000
			Japan	57,000
			Belgium-Luxem- burg E.U.	50,500
Finland	..	..	United Kingdom	515,500
			United States	255,200
			France	105,600
Canada	..	..	United States	454,200
Norway	..	..	United States	108,800
			United Kingdom	62,100
			Japan	56,700
United States	..	..	Japan	156,200
Austria	..	..	Italy	88,900
Germany	..	..	United States	67,700
WORLD'S EXPORTS RE- PORTED			..	4,756,100
WORLD'S IMPORTS RE- PORTED			..	4,393,900

\* Including vegetable fibres and rags.

This industry was severely dislocated in World War II. The potential picture of world trade in wood pulp can, however, be viewed by examination of the accompanying reports for the year 1936. The production for that year in the United States was :

Mechanical pulp .. ..	1,500,000 short tons
Sulphite pulp .. ..	1,800,000 " "
" Sulphate " pulp .. ..	1,800,000 " "
" Soda " pulp .. ..	400,000 " "

to which there should be added the imports of paper to complete the U.S.A. picture, namely, 2,750,000 short tons of newsprint of which about 90 per cent. came from Canada.

**WOOD SPIRIT** — See Wood (Distillation), and Alcohols (Methyl).

**WOOD SUGAR** — See Glucose, Sugar, and Wood.

**WOOD TURPENTINE** — See Pine Oil, and Turpentine.

**WOOD'S FUSIBLE METAL** — See Alloys, and Bismuth.

**WOOL** — The cleansed fibres from sheep and goat skins, of which the outstanding chemical constituent is keratin. It is of a protein character and is related to horn, containing from 49 to 52 per cent. carbon, 6·8 to 7·2 per cent. hydrogen, 20 to 21 per cent. oxygen, 18 to 19 per cent. nitrogen, and about 3·22 to 3·4 per cent. sulphur. Wool contains fat (up to about 2 per cent.) and some cholesterol, also both aliphatic and aromatic amino groups (the total amino-nitrogen being probably about 0·7 per cent.), and is decomposed by hot caustic alkaline solutions. Persoz' reagent (see same) does not dissolve wool.

The fat or grease found in wool, known as "suint," occurs to the extent of 20 ounces per fleece of 9 pounds, and of this quantity about one-third is potash. It is one of the best preventives of rust, and is particularly valuable for use in respect of machinery which is standing. In a refined state it is used in the preparation of "lanolin," and can be used for soap-making. In another refined state it is known as wool wax, of sp. gr. 0·94, m.p. 35° C., sap. v. 102, i.v. 25, and ref. ind. 1·48.

Woollen fabrics are liable to attack by certain bacteria, including *B. subtilis* and *B. mesentericus*, causing a swelling of the fibres, loss of natural twist, and later, the loss of tensile strength; they also suffer damage by exposure to light and air, and by attack of the clothes moth.

Emulsions of 90 parts carbon tetrachloride and 90 parts tetrachlorethylene are used industrially under the names of "Hexoran" and "Trioran" for the cleansing of raw wool, as also another preparation named "Perpentol."

With respect to the bleaching of wool it has been found that when sulphur dioxide and alkali are present in particular proportions they assume a special phase of activity in effect and economy, while the fabrics treated in this way better retain their white bleached appearance even after successive washings. (See Report of Advisory Council, Department of Scientific and Industrial Research for 1929-1930 (H.M.

Stationery Office).) High sulphur content means high resistance to deterioration of wool during chemical treatment.

At the Government Wool Disinfection Station at Liverpool, wool is disinfected after some preliminary preparation by a ten minute exposure at 102° F. (39° C.) to the action of a dilute alkaline solution in order to remove albuminous matters, followed by further twenty minute treatment with a dilute alkaline soap solution at 102° F. (39° C.) to promote a susceptible state of any spores contained in the wool, and subsequently passed through successive baths of a 2 to 3 per cent. solution of formaldehyde, the material being squeezed between rollers at each stage to remove the several liquids.

According to S. R. Trotman and R. W. Sutton, scoured wool exposed to air but protected from light is stated to be liable to become acid in reaction and suffer surface damage, so that the loss on subsequent scouring becomes very high. It is found to be infected with a number of bacterial and fungicidal growths, and has an affinity for dyes differing from that of the undamaged material, the bacterial damage being attributed to damp storage. Sodium fluosilicate has been found notably efficient as an antiseptic in respect of mildew growths on wool. (See Fungicides, and Insecticides.)

Wools are **graded** by feel and diameter of fibre, and there are tests for the various qualities. Olive and other oils are ordinarily employed in their preparation and working, the lubrication facilitating the passage of the fibres over each other in combing and carding.

See Adeps Lanæ, Degras, Nylon, and "Orlon."

**WOOL ALCOHOLS** — The steroid alcohols prepared from wool fat by saponification and separation of the unsaponifiable fraction, containing not less than 28 per cent. of cholesterol with agnosterol, lanosterol, and triterpene alcohols. The product is a golden brown solid, brittle when cold but becoming plastic on warming; soluble in ether, chloroform, and light petroleum; m.p. about 54° C.; it is an emulsifying agent, promoting the formation of water-in-oil emulsions, and is used in medicine as a constituent of emulsified ointment bases.

**WOOL FAT** — See Waxes.

**WOOL PITCH** — See Pitch.

**WORMSEED OIL** — See Chenopodium Oil.

**WORMWOOD OIL** — A volatile oil obtained by distillation from the leaves and flowering tops of *Artemisia Absinthium*. The oil is green in colour and contains thujone, thujyl alcohol, and acetate, with phellandrene and probably pinene; soluble in alcohol and ether; sp. gr. 0.925 to 0.960 at 15° C.; ref. ind. about 1.460 at 20° C.; used in making absinthe. (See Tarragon Oil.)

**WORT** — The liquid product resulting from the mashing of cereal grains (such as barley, rye, and maize, with malt), containing maltose, iso-maltose, dextrine, etc. (See Alcohol, Beer, and Whisky.)

**WULFENITE** — Crystalline lead molybdate ( $\text{PbMoO}_4$ ), of crystal system No. 2, and sp. gr. 6 to 7, found in the United States, etc. (See Molybdenum.)

**WURTZITE** — A native variety of zinc sulphide found in the form of hexagonal prisms in Montana, Utah, etc.; used in making paints and luminous paint.

**X-RAYS (Röntgen Rays)** — A form of ultra-violet light given off from the cathode when passing an electric current of high voltage (in the neighbourhood of 100,000 volts) through a highly vacuous glass tube and deflecting the rays by a metallic mirror. These waves are invisible to the eye; are 10,000 times shorter than those of light (50 to 0.05 millimicrons); cannot be reflected from mirrors or concentrated by use of lens. By their use examination can be made of things 10,000 times smaller than with a microscope. They have the power of penetrating solid substances such as animal tissues, paper, wood, and some metals, and by action on a photographic plate behind the object to be "radiographed," it is possible to obtain shadowgraphs of portions of the human skeleton, the bones being not so easily penetrated as are the skin, muscle, etc.

Studies by X-ray have proved of great value in the examination of the structure of ice, graphite, the diamond and other crystals, and the atomic or molecular arrangements in three dimensions of many organic compounds. They are also employed for determining the structure of cellulose, fibres, etc., and find industrial application for the detection of blow-holes and cracks in metals, brazings, and heavy castings; the toughening of varnish on patent leather so that it is made more pliable; the detection of substances by their X-ray spectra; the examination of ferro-concrete, and internal parts of clocks, watches, motor tyres, electric cables, cricket and golf balls; and the atomic arrangement of metals and alloys. In surgery they are successfully used for locating bullets, etc., in the human body, for indicating the nature of fractures, and distinguishing between strains and dislocation.

The fundamental law of X-ray spectra was discovered by the late H. G. J. Moseley, who also provided the foundation for X-ray analysis. (See Atoms (Moseley's Atomic Numbers).)

*References:* Bragg and Shearer on "Applications to Chemical Industry" (Lecture, Society of Chemical Industry, April 4, 1932); "A Decade of Applied X-Ray Research," address by G. L. Clark (*Chem. and Ind.*, 52, 317, 336 (1933)); *X-Rays and Electrons*, by A. H. Compton (Macmillan and Co., London and New York); *Rays and X-Rays*, by V. E. Pullin (Ernest Benn, London); *X-Ray Spectroscopy*, by M. Siegbahn (Oxford University Press); *Applied X-Rays*, by G. L. Clark (McGraw-Hill Book Co., New York); *Concerning the Nature of Things*, by W. H. Bragg (Harper and Brothers, New York); *X-Rays*, by G. W. C. Kaye (Longmans, Green and Co., New York); *Chemical Analysis by X-Rays*, by G. von Hevesy (McGraw-Hill Book Co.,

New York); *An Introduction to X-Ray Metallography*, by A. Taylor (Chapman and Hall, London); *X-Ray Crystallography*, by M. J. Buerger (John Wiley and Sons, New York); *Structure of Metals*, by C. S. Barrett (McGraw-Hill Book Co., New York); *The Physical Examination of Metals*, Vol. II, by B. Chalmers and A. G. Quarrell (Longmans, Green, and Co., New York); also Atoms, Electrons, Radioactivity, Stereochemistry, Ultra-violet Rays, and Wave Lengths.

**XANTHATES** — Salts of xanthic acid (ethylhydrogen dithiocarbonate) ( $\text{C}_2\text{H}_5\text{O.CS.SH}$ ), such as potassium ethyl xanthate ( $\text{C}_2\text{H}_5\text{O.CS.SK}$ ).

Cellulose xanthates are made by the action of carbon disulphide on the sodium derivative of cellulose, and form colloidal solutions from which viscose (see same) is prepared.

**XANTHENE DYESTUFFS** are derivatives of xanthene  $\left( \begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \\ | \quad \quad | \\ \text{O} \end{array} \right)$ .

**XANTHINE (2,6-Dihydroxypurine)** ( $\text{C}_5\text{H}_4\text{O}_2\text{N}_4$ ). The parent compound from which certain purine bases are derived, such as caffeine, theobromine, and theophylline. These are all methyl derivatives of xanthine.

**XANTHIUM ECHIFATUM** seeds are stated to contain 30.7 per cent. kernels, which yield 29.9 per cent. oil, having i.v. 140.8 and sap. v. 190.2, but the press cake contains some toxic principle which renders it harmful to cattle.

**XANTHOPHYLL** ( $\text{C}_{40}\text{H}_{56}\text{O}$ ) — One of the four constituents of ordinary chlorophyll. (See Chlorophyll, and Plant Colouring Matters.)

**XENON (Xe)** — Atomic weight, 131.3. See Elements for other data. One of the rare gases of the atmosphere, belonging to the argon group. It is recovered in the heavier portion of liquefied air, and is calculated to be present to the extent only of 6 parts by volume in 100,000,000 parts of air. (See Air.)

**XENYL** — The monovalent radical  $-\text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_5$  of diphenyl.

**XEROFORM** — Bismuth tribromophenylate.

**XYLAN** — A pentosan made up of *d*-xylose units linked in the 1- and 4-positions. It is associated in nature with and closely related to polyglucuronic acid from which xylan can be made by loss of carbon dioxide.

**XYLENE (Xylol)** ( $\text{C}_6\text{H}_4(\text{CH}_3)_2$ ) — Isomeric benzenoid hydrocarbons of the benzene group present in coal naphtha, of faint odour distinct from that of benzene, constituting a large proportion of so-called "naphtha solvent," and as such used as a raw material in the manufacture of dyes, also as a wetting and grease-dissolving agent in scouring baths. There are three isomeric xylenes, that from coal tar consisting of a mixture of all three kinds. *Ortho*-xylene of sp. gr. 0.8802 boils at  $144.4^\circ\text{C}$ ., *meta*-xylene, sp. gr. 0.8642, b.p.  $139.1^\circ\text{C}$ ., and *para*-xylene, sp. gr. 0.8610, b.p.  $138.3^\circ\text{C}$ .; they can be extracted from crude xylol, and are all colourless, mobile liquids, soluble in alcohol and ether. (See Coal, and Naphtha.)

**XYLENOLS** ( $(\text{CH}_3)_2\text{C}_6\text{H}_3(\text{OH})$ )—Phenolic compounds (dimethylhydroxybenzenes or dimethylphenols) of high boiling-point, of which some six modifications are known, forming part of the constituents of so-called "phenoloids" from blast furnaces, and used in the manufacture of powerful disinfectants.

**XYLIDINES** ( $\text{C}_6\text{H}_3(\text{CH}_3)_2(\text{NH}_2)$ )—Six isomeric amines, all liquids, except the 3,4-dimethylaniline, and used in the manufacture of dyestuffs.

**"XYLOLITH"**—A building material and flooring composition made from sawdust by the interaction of magnesia and magnesium chloride, producing thereby the magnesium hydroxide in a colloidal form, which cements the mixture; it is made in the forms of slabs and tiles, which are weather-resistant and fireproof. (See "Necol," and "Sorel Cement.")

**XYLONITE**—See Celluloid.

**XYLOSE** ( $\text{CH}_2\text{OH}(\text{CHOH})_3\text{CHO}$ )—An aldopentose that is stereoisomeric with arabinose, ribose, and lyxose. Xylose is obtained by hydrolysis with dilute acid of xylan present in cottonseed hulls (40 per cent.), corn cobs (32 per cent.), peanut shells (26 per cent.), and other agricultural wastes. Xylose has been used as the source of synthetic vitamin C. (See *An Introduction to the Chemistry of Carbohydrates*, by Honeyman (Cambridge Univ. Press); and Pentoses.)

**XYLYL**—The univalent radical ( $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2-$ ) derived from *o*-, *m*-, or *p*-xylene.

**XYLYLENE**—The divalent radical ( $-\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2-$ ) derived from *o*-, *m*-, or *p*-xylene.

**YACCA GUM**—See Gums and Resins.

**YAM**—A genus of plants (*Dioscorea*, N.O. Dioscœraceæ) natives of W. Indies, Polynesia, China, etc., of which the fleshy roots containing much starch are used as food after boiling. There are some 150 species, of which varieties are cultivated in Asia, Africa, and America, the *Tamus* (*Testudinaria*) *elephantipes* (a S. African variety) being the so-called Hottentot's Bread.

**"YATREN"**—See Chiniofon.

**YEASTS**—The yeasts belong to the great family of the fungi. Ordinary cultivated yeast (*Saccharomyces cerevisiæ*) consists of microscopic round or oval vegetable cells of about  $\frac{1}{3000}$  inch in diameter, 1 ounce containing about 50,000 million cells. These multiply by gemmation (budding), and are employed in various processes of fermentation—wines, beers, and spirits—as also in bread-making. Fermentation induced by yeast can only take place between 3° and 35° C., and the organism is killed by a greater alcoholic strength than represented by

a solution of 14 per cent. alcohol. The process of fermentation is independent of the cell walls, and is due to one of several enzymes (termed zymase) present in their contents, and which can be extracted by disintegration and subjection of the yeast cells to hydraulic pressure. All fermentations effected by living yeast proceed more slowly than when induced by yeast preparations, and most if not all are accelerated by potassium phosphate. Yeast loses its activity when dried and heated to 60° C. or exposed to the action of antiseptics.

The hexoses alone are directly fermentable by zymase, and of these only four, namely, *d*-glucose, *d*-mannose, *d*-galactose, and *d*-fructose; other sugars, such as maltose and cane sugar, having first of all to be converted into one of these; but certain yeasts which secrete invertase are capable of fermenting cane sugar. Some yeasts secrete both invertase and maltase, which latter can ferment maltose.

There are many varieties of yeast of distinctive properties. *S. cerevisia* is the ferment used in beer-making, while the wild yeast, *S. ellipsoideus*, is the wine ferment. There is a certain small amount of fat in the normal yeast cell, which, together with the sterols including ergosterol ( $C_{27}H_{42}O$ ) associated with it, are derived from carbohydrate materials consisting of glycogen and mannan (Daoud and Ling). These are held in combination in the cell, and build up with some complex, which is broken down by acid hydrolysis. Yeast is stated to contain a certain proportion of the B vitamin, while ergosterol is the parent substance of vitamin D.

Industrially, brewers' yeast is prepared from a wort made from barley, rye, maize, and other cereals, in which the conversion of the carbohydrates to maltose has been pushed as far as possible by seeding with a yeast culture. There are a number of modified processes of this sort which give other varieties.

"Aeration yeast" or "air yeast," as used for bread-making, is prepared under a carefully controlled process of nutrition and aseptic conditions from agar using the right kind of pure culture and aeration of the fermenting mash. (See lecture by J. Vargas Eyre (Institute of Chemistry, November, 1931), on the "Fermentation Industries.")

A number of useful articles are prepared from yeast, including nucleic acid, and a bakelite-like substance named "Ernolith" (see same) of plastic character. Dry yeast contains some 50 per cent. proteins, and is a valuable source of vitamins. Brewery yeast has a considerable food value, and a food named "Marmite" is prepared from it resembling meat extract in flavour. "Katazymans" is a German food made from yeast by plasmolysis—that is, shrinking of the cells by placing in a solution of about 66 per cent. sugar carbohydrates and 33 per cent. yeast constituents.

A process is available for inoculating waste liquors from sugar refineries, distilleries, paper and starch works, with a particular variety of yeast which grows quickly and does not produce alcohol. This increases in quantity at the expense of the carbohydrates in the waste water and added ammonium salts, and is ultimately separated and dried. It is stated that 100 parts of sugar or its equivalent present

in the waste, and 37.5 parts of nutritive ammonium salts, yield 150 parts of compressed yeast, which, after drying, contains from 40 to 60 per cent. of albuminous matter. This dried yeast, rich in nitrogenous matter, is used as cattle fodder. (See C. N. Frey *et al.* on "Yeast, Physiology, Manufacture, and Use" (*Ind. Eng. Chem.*, **28**, 879 (1936)); also Barm, Enzymes, Ergosterol, Invertase, Proteins, Sterols, Vitamins, and Zymase.)

**YELLOW WOOD** — See Fustic Extract.

**YEW** (*Taxus*, N.O. Taxaceæ) — A genus of which species are widely distributed. The common yew is *Y. baccata*; the wood is very hard and nearly equal to box for making fine work.

**YLANG-YLANG OIL** (*Cananga Java Oil*) — A yellow essential oil distilled from the flowers of *Unona odoratissima* (*Cananga odorata*), a tree indigenous to the Malay Archipelago and cultivated in the Philippines. There are several varieties of the oil which are known as "cananga" and "manila" oils. It contains methyl and benzyl acetates, linalool, geraniol, and eugenol; sp. gr. 0.910 to 0.940 at 15° C.; ref. ind. 1.494 to 1.505 at 20° C.; opt. rot.  $-37^\circ$  to  $-45^\circ$  at 20° C.; these constants may vary with the source of the oil. Cananga oil, distilled from *Cananga odorata* in Java, differs in composition from the oils produced in Manila, the former containing fewer esters and more sesquiterpenes. Ylang-Ylang oils are used in perfumery.

**YOHIMBINE** ( $C_{21}H_{28}O_3N_2$ ) — A crystalline poisonous alkaloid of m.p. 235° C., extracted from Yohimba bark, *Pausinystalia yohimba*, probably identical with quebrachine obtained from white quebracho bark. It has been used as an aphrodisiac. (See *The Plant Alkaloids*, by Henry (Cambridge Univ. Press).)

**YOUNG FUSTIC** — The heartwood of a sumac (*Rhus cotinus*) used in the leather industry. (See Fustic Extract.)

**YOUNG'S MODULUS** — See Modulus of Elasticity.

**"YPERITE"** — See Mustard Gas.

**YTTERBIUM** (Yb) — Atomic weight, 173.04. See Elements for other data. Ytterbium is one of the rare-earth elements and a member of the yttrium group of the same, found in the mineral *gadolinite* (*ytterbite*) and associated with yttria.

**Ytterbium oxide** ( $Yb_2O_3$ ) is a white solid; the **chloride** ( $YbCl_3 \cdot 6H_2O$ ) a green solid; and the **sulphate** ( $Yb_2(SO_4)_3$ ) a colourless solid; the two last are soluble.

**YTTRITE** (*Ytterbyte*, *Gadolinite*) — A mineral containing silicates of beryllium, yttrium, and other rare earths. (See *Gadolinite*.)

**YTTRIUM** (Y) and its Compounds — Atomic weight, 88.92. See Elements for other data. Yttrium is one of the rare-earth elements giving its name to one of the two groups of the same. It is found in *fergusonite*, *gadolinite* (*ytterbite*), *xenotime*, and *samaraskite*, and (like ytterbium) is associated with the boron group of elements. It is commonly described as a greyish-black powder which is capable of decomposing water to

some slight extent at the ordinary temperatures and more rapidly when heated, forming the oxide ( $Y_2O_3$ ), from which the metal can be obtained. Prepared by electrolysis of the fused chloride mixed with a small quantity of sodium chloride, it is obtainable in coherent form, bright, lustrous, highly crystalline, and not malleable. It is very soluble in acids.

**Yttrium oxide** ( $Y_2O_3$ ) is a pale yellow solid; the **chloride** ( $YCl_3 \cdot 6H_2O$ ) a reddish deliquescent solid; the **sulphate** ( $Y_2(SO_4)_3 \cdot 8H_2O$ ) a reddish slightly soluble solid; the **nitrate** ( $Y(NO_3)_3 \cdot 6H_2O$ ) a reddish deliquescent solid; the **hydroxide** ( $Y(OH)_3$ ) and the **carbonate** ( $Y_2(CO_3)_3 \cdot 3H_2O$ ) are pale yellow insoluble solids.

The compounds of yttrium closely resemble the corresponding aluminium compounds.

The **yttrium group** of the rare-earth elements consists of the elements yttrium itself, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium, the potassium sulphate compounds of all of which are soluble or comparatively soluble in water. See Cerium for the other group of rare-earth elements, and the individual members.

**YTTROTANTALITE** — A rare mineral ( $Y_4(Ta_2O_7)_3$ ), of sp. gr. 3.3. (See Erbium.)

**"ZAMAK" ALLOYS** — A series of die-casting alloys containing approximately 4 per cent. aluminium, up to 3 per cent. copper, 0.02 to 0.06 per cent. magnesium, and the remainder electrolytic zinc.

**ZANZIBAR** — See Gums and Resins (Anime, and Copal).

**ZARATITE (Emerald Nickel)** — An amorphous, hydrous, basic nickel carbonate ore ( $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ ) occurring in Maryland, U.S.A., etc., of sp. gr. 2.5.

**"ZEANIN"** — A maize flour, practically free from oil and protein, and preferable to maize grits for brewing, giving a higher yield of extract.

**ZEOLITE PROCESSES (Water Softening)** — See Water Conditioning.

**ZEOLITES (Zeoliths)** are natural mineral deposits of an opaque, vitreous character abundantly diffused in nature, and generally found in amygdaloidal cavities or fissures of basalt and certain crystalline schists, described as double hydrated silicates of aluminium and calcium (or sodium). When treated with acids they partially dissolve, leaving the silica in a gelatinous state. *Stilbite*, *natrolite*, and *analcite* are three zeolites. (See also "Doucil," and Water Conditioning.)

**"ZEPHIRAN"** — Benzoyl trimethylammonium bromide, a powerful bactericide.

**"ZERLATE"** (Du Pont) — Trade-mark for a fungicide based on zinc dimethyldithiocarbamate. Used for the control of early blight on potatoes, leaf spot on tomatoes, brown rot on peaches, and septoria on celery.

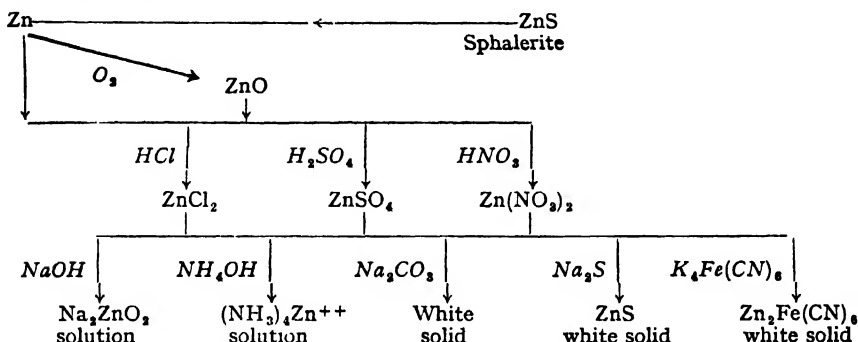
**ZERO (Absolute)** — Minus  $273.16^{\circ}\text{C}$ . "The absolute zero is probably the most important singularity in nature" (John F. Allen in *Scientific American*, July, 1949, p. 29). (See Heat (Notable Temperatures), and Helium.)

**"ZICRAL"** — A high-strength aluminium base alloy containing 7 to 8.5 per cent. zinc, 1.75 to 3 per cent. magnesium, 1 to 2 per cent. copper, 0.1 to 0.4 per cent. chromium, 0.1 to 0.6 per cent. manganese, 0.7 per cent. iron, and some silicon. It can be rolled, drawn, forged, and used as a clad metal. (See M. Tournaire, in *Rev. de l'Aluminium*, 23, 303 (Oct. 1946).)

## ZINC-CONTAINING SUBSTANCES

## CHART SHOWING PRINCIPAL INTER-RELATIONSHIPS

Arranged by the Editor



**ZINC (Zn) and its Compounds** — Atomic weight, 65.38. See Elements for other data. Zinc is not met with in nature in the metallic state, but occurs as *calamine* or *zinc spar* (zinc carbonate) in Silesia, the United States, and Belgium. *Blende* (*sphalerite* or zinc sulphide) is found and worked in the U.S.A., and to some extent in England, while in New Jersey (U.S.A.) *zincite* (zinc oxide) (the reddish colour of which is due to manganese) is found in considerable amount. Zinc also occurs in *franklinite* (a compound oxide of zinc and iron), in *gahnite* (*zinc spinel*, a zinc aluminate), in *smithsonite* (zinc silicate), and other mineral forms.

The natural zinc carbonates readily yield the oxide by calcination :  $\text{ZnCO}_3 = \text{ZnO} + \text{CO}_2$ .

Zinc is a bluish-white crystalline metal, and only tarnishes slightly in moist air. It is brittle at ordinary temperatures, but ductile at  $100^{\circ}$  to  $150^{\circ}\text{C}$ ., and can then be rolled into sheets and drawn into wire. At  $100^{\circ}\text{C}$ . the specific gravity of zinc changes from 7.14 to about 7.10, suggesting that there are at least two allotropic forms of zinc. At  $200^{\circ}\text{C}$ . zinc is brittle and can be powdered. Its melting point is  $419^{\circ}\text{C}$ ., and its boiling point  $907^{\circ}\text{C}$ . It is used in making brass, it forms alloys with tin, copper, and antimony in all proportions, and is a component part of many other alloys containing lead and bismuth (See Alloys.)



the bulk of which is made directly from the ores *franklinite* and *zincite*, of which large deposits occur in New Jersey, whereas the English make is either from *calamine* or *speller*.

**Zinc Hydroxide** ( $\text{Zn}(\text{OH})_2$ ), which is produced in a white flocculent form when an alkaline hydroxide is added to a solution of a zinc salt, is soluble in an excess of alkali, sodium hydroxide yielding sodium zincate ( $\text{Na}_2\text{ZnO}_2$ ), and ammonium hydroxide yielding tetra-ammonio-zinc ion ( $(\text{NH}_3)_4\text{Zn}^{++}$ ). It can be obtained in crystalline form.

**Zinc Acetate** ( $\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$ ) is a white crystalline salt, soluble in water, and used as a mordant in dyeing.

**Zinc Carbonate** ( $\text{ZnCO}_3$ ) in dry form is a white amorphous powder, insoluble in water, and used as a pigment and in medicine, whereas *Zinci carbonas* of the Pharmacopœia is a basic compound having the composition expressed by  $\text{ZnCO}_3 \cdot 2\text{Zn}(\text{OH})_2 \cdot \text{H}_2\text{O}$ .

**Zinc Chloride** ( $\text{ZnCl}_2$ ) is prepared by dissolving the metal in hydrochloric acid and concentrating to that state in which it solidifies upon cooling, when it is cast into sticks. It is a deliquescent soft compound, m.p.  $262^\circ \text{C}$ ., b.p.  $732^\circ \text{C}$ ., very soluble in water, and can be distilled without decomposition. Commercially it is also prepared in the form of a strong solution of  $102^\circ \text{Tw}$ ., and used as an antiseptic cotton-sizing ingredient and otherwise in the textile industries, also in connection with soldering, and as a wood preservative. It can be prepared in anhydrous form by action of chlorine upon metallic zinc at  $500^\circ \text{C}$ .; also by passing phosgene or a mixture of carbon monoxide and chlorine into a mixture of zinc oxide-containing material and molten zinc chloride at  $400^\circ \text{C}$ . A paste consisting of a mixture of the chloride with zinc oxide is employed in dentistry, under the name of "oxy-chloride," as a stopping for teeth. It forms double salts with other chlorides such as  $\text{ZnCl}_2 \cdot \text{NH}_4\text{Cl}$  and  $\text{ZnCl}_2 \cdot 2\text{KCl}$ .

**Zinc Chromate** ( $\text{ZnCrO}_4$ ) is a yellow crystalline substance, insoluble in water, and finds increasing use as a pigment and catalyst. It is made by action of chromic acid on zinc hydroxide, and commercially in a basic form by dissolving zinc oxide in sulphuric acid and precipitation with an excess of sodium dichromate at about  $50^\circ \text{C}$ . (See Zinc Yellows.) **Zinc Dichromate** ( $\text{ZnCr}_2\text{O}_7$ ) is an orange-coloured substance, insoluble in water, and used as a pigment.

**Zinc Cyanide** ( $\text{Zn}(\text{CN})_2$ ) — A white poisonous powder, insoluble in water, but soluble in dilute mineral acids, made by precipitation from a soluble zinc salt with potassium cyanide solution. It reacts with excess potassium cyanide to form soluble  $\text{K}_2(\text{Zn}(\text{CN})_4)$ .

**Zinc Fluoride** ( $\text{ZnF}_2$ ) is a white powder, insoluble in water, used in the ceramic industries.

**Zinc Iodide** ( $\text{ZnI}_2$ ) can be prepared by the interaction of zinc sulphate and barium iodide, the solution resulting after filtration being evaporated and crystallized. For process work, it is prepared also by the direct action of iodine upon metallic zinc and dissolving the product in water.

**Zinc Laurate** produces a desirable lather in soap, is a useful accelerator in rubber, and retards the yellowing of white kid leather. It can be made practically only from coconut and palm kernel oils.

**Zinc Nitrate** ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) is a white crystalline salt, soluble in water, and used to some extent in medicine.

**Zinc Sulphate** is manufactured by roasting the mineral sulphide in air under certain careful conditions and dissolving out the sulphate thus produced; also by dissolving the metal in dilute sulphuric acid. It crystallizes in monoclinic form as  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ , is very soluble in water, and somewhat efflorescent. The monohydrate ( $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ ) becomes anhydrous upon heating to about  $300^\circ\text{C}$ ., and is decomposed at a higher temperature into sulphur dioxide, oxygen, and zinc oxide. It is a particularly poisonous salt, and finds use in medical practice as an antiseptic, also as an astringent preservative agent for wood and skins, as a mordant in calico-printing, and as a weed-killer. It has been stated that more than 20 per cent. of the world's production of zinc is made by the electrolysis of zinc sulphate.

**Zinc Sulphide** ( $\text{ZnS}$ ) is found native as *sphalerite* and *wurtzite*. When precipitated from a solution of a zinc salt by addition of an alkaline sulphide solution, it is a practically white amorphous substance, insoluble in water and acetic acid, and is used to some extent as a luminous agent, also as a pigment in place of white-lead. If prepared of chemical purity the sulphide is stated to exhibit little or no phosphorescence, but the introduction of a very minute quantity of copper or manganese chloride or some other heavy metallic salts produces a fine glow; when it contains as little as 0.00006 gram copper and is heated to redness it exhibits a beautiful phosphorescence. The preparation of the activating mixture and the phosphorescent product is described by R. Rhode (*C.T.J.*, 86, 502 (1930)). A mixture of the sulphide containing 1 to 30 per cent. cadmium sulphide is stated to exhibit a much greater luminescence under X-rays than ordinary zinc sulphide. (See *C.T.J.*, 90, 283 (1932).)

Irradiated by bombardment with alpha rays from radium, zinc sulphide crystals are used to coat the faces of watches and compass cards, so that they are visible in the dark. Phosphorescent zinc sulphide is obtained as a white spongy mass of wurtzite crystals when an intimate mixture of finely pulverized zinc and sulphur is exploded by shock, heat, or friction.

**Zinc Sulphite** ( $\text{ZnSO}_3 \cdot 2\text{H}_2\text{O}$ ) — A white crystalline powder made by the action of sulphurous acid on zinc hydroxide; used as an anatomical preservative, and in sugar refining as a decolourizing agent.

**Zincates**, such as potassium zincate ( $\text{K}_2\text{ZnO}_2$ ), are made by treating zinc metal or zinc hydroxide with potassium hydroxide solution.

All the soluble salts of zinc are poisonous.

**ZINC BLENDE** — See Zinc, and Sulphur.

"**ZINC FORMOSUL**" is described as basic zinc formaldehyde-sulphoxylate, being a greyish-white powder, insoluble in water, but which exercises reducing power when boiled with very dilute acids, or at high temperatures in their absence. It can be used in the autoclave and "Twitchell" processes of fat splitting, and is stated to assist in the bleaching of the resulting glycerol.

**ZINC WHITE** — Zinc oxide of various degrees of purity. (See also Paints (Orr's Zinc White).)

**ZINC YELLOW** — Zinc chromate pigment.

**ZINEB (Zinc Ethylene-bis-Dithiocarbamate)** — A fungicide.

**ZINGERONE** — See Ginger.

**"ZINNATINE"** — The name given to what is described as a non-poisonous acid-resisting gold coating for the insides of food containers and closures capable of resisting all blackening stains.

**ZIRAM (Zinc Dimethyldithiocarbamate)** — A fungicide.

**ZIRCONIUM (Zr) and its Compounds** — Atomic weight, 91.22. See Elements for other data. Zirconium occurs in so-called *zircons*, that is, silicate ( $\text{ZrSiO}_4$ ), in Norway, Ceylon, and Madagascar, while as oxide ( $\text{ZrO}_2$ ) it is found in Brazil and Ceylon as *brazilite* or *baddeleyite* (a mineral of crystal system No. 5, and sp. gr. 5 to 6) containing about 96.5 per cent.  $\text{ZrO}_2$ ; it is also found in association with other metals in various *columbates*. Another Brazilian deposit, known as *orvillite*, is said to contain about 72 per cent.  $\text{ZrO}_2$ . *Zirkite* is light grey to black in colour, and varies in sp. gr. from 4.8 to 5.2; it is stated to be a mixture of brazilite, zircon, and another silicate of zirconium. Both brazilite and zirkite are employed as refractories in the compounding of zirkite bricks and cements, after freeing them from the associated oxides of iron, aluminium, and titanium by boiling in hydrochloric or sulphuric acid. Approximately 10,000 tons per year of zircon is produced in Australia, and 5,000 in Brazil.

As obtained by reduction from its oxide ores, zirconium is a black amorphous powder, and when agglomerated by fusion it presents a steel-grey appearance. It can be obtained both from zirconium chloride and potassium zirconium fluoride by the action of metallic sodium. According to A. E. van Arkel and J. H. de Boer it can be obtained in pure form by passing the vapour of the iodide over a heated tungsten filament, as a thick layer thereon. It can also be deposited on zinc when that metal is placed in a solution of zirconium sulphate in methyl alcohol (H. S. Gable), and another process is the aluminothermic reduction of the oxide. (See *Strategic Minerals*, by J. B. De Mille (McGraw-Hill Book Co., New York), and *Rarer Metals*, by J. De Ment and H. C. Dake (Chemical Publishing Co., Brooklyn, N.Y.).)

Zirconium forms alloys with copper, gold, and nickel at high temperatures, and a silvery white, crystalline alloy of zirconium with aluminium has been prepared of the composition  $\text{Zr}_3\text{Al}_4$ . It belongs to the same group of elements as titanium, is a good conductor of electricity, fairly soft and ductile when pure, and does not easily tarnish in the air unless heated, when it oxidizes slowly. It is almost free from attack by acids, excepting aqua regia, and hydrofluoric acid, and when heated to redness, combines readily with chlorine, nitrogen, and oxygen.

During World War I, zirconium in small amount (0.34 per cent.) was introduced into the steel used by the French in making armour-plate, as in association with 3 per cent. of nickel it was found to add to

its tensile strength. It is also used as a constituent of the alloy named "Cooperite." Zirconium dissolves in zinc to the extent of 0.02 per cent. at 400° C. with eutectic at 0.1 per cent. zirconium and 416° C.

Zirconium has a greater affinity for oxygen at high temperatures than silicon has, and for this reason a greatly increased content of silicon in finished steel can be obtained by its use, while at the same time it is efficient in removing the final traces of oxygen and nitrogen from the steel. The zirconium is oxidized, and together with the oxides of silicon and manganese is completely removed as fusible slag.

**Zirconium Oxide (Zirconia)** ( $\text{ZrO}_2$ ), stated to exist in three polymorphic forms, is obtained by heating the hydroxide  $\text{Zr(OH)}_4$ , has m.p. of 2,700° C., and is a heavy, insoluble, white, amorphous powder of sp. gr. 5.7. It is a valuable refractory material for resistance to high temperature, being used as crucibles in which to melt pure iron, platinum, and tungsten alloys, and as linings for the hearths of steel furnaces; is a good abrasive material; and is used in the preparation of acid-proof enamels, and in the manufacture of special glasses, its employment, among other properties, enhancing resistance of glass to attack by alkaline solutions. Zirconia has a very low coefficient of thermal expansion. X-ray diffraction studies of zirconium oxide are described by G. L. Clark and D. H. Reynolds in *Ind. Eng. Chem.*, 29, 711 (1937).

**Zirconium Acetate** ( $\text{Zr(C}_2\text{H}_3\text{O}_2)_3\text{OH}$ ) is a white, crystalline, soluble salt, used for weighting silk.

**Zirconium Carbide** ( $\text{ZrC}_2$ ) decomposes water and finds use as an abrasive. (See Abrasives.)

**Zirconium Carbonate (Basic) (Zirconyl Carbonate)** ( $\text{ZrOCO}_3$ ) is a white insoluble compound, prepared by interaction of a soluble zirconium salt and a solution of sodium carbonate, and from it the oxide can be made.

**Zirconium Hydroxide** ( $\text{Zr(OH)}_4$ ) is a white, bulky compound, insoluble in water, prepared by precipitation from a soluble zirconium salt, using a solution of sodium hydroxide.

**Zirconium Nitrate** ( $\text{Zr(NO}_3)_4 \cdot 5\text{H}_2\text{O}$ ), and **Zirconium Sulphate** ( $\text{Zr(SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ) are both soluble salts, and **Zirconium Chloride** ( $\text{ZrCl}_4$ ) is decomposed with water into **Zirconyl Chloride** ( $\text{ZrOCl}_2$ ), which is used in tanning.  $\text{ZrCl}_4$  is soluble in ethanol.

**Zirconium Silicate** is a white insoluble substance, used as a pigment in paints and cosmetics.

Zirconium salts are very basic in character, and in solution have a tendency to undergo hydrolysis, and to pass into a more or less colloidal state.

Compounds of zirconium resemble the corresponding compounds of thorium and of silicon.

(See "Zirconia and Its Industrial Applications," by W. O. R. Wynn (*Ind. Chem.*, 9, 237 (1933)); *Zirconium and Its Compounds*, by F. P. Venable (Reinhold Publishing Corp., New York); *Analytical Methods for Certain Metals*, by R. B. Moore *et al.* (U.S. Bureau of Mines, Bulletin 212, Superintendent of Documents, Washington); and Hafnium.)